THE UNIVERSITY OF ALBERTA

THE PREPARATION AND REACTIONS OF SOME ALKALI METAL DERIVATIVES OF FLUORENE

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A B S T R A C T

The metalation of fluorene by alkali metals and the reactions of the organometallic derivatives of fluorene with alkyl halides, deuterium oxide and benzoyl chloride have been studied. An investigation of the infrared spectra of fluorene and its C_9-substituted derivatives was made.

The infrared bands at 2901, 2885, 1400,1298, 952 and 692 cm^{-1} in the spectrum of fluorene could be associated with the methylene group. The bands at 974, 827 and 667 cm^{-1} in the spectra of deuterated fluorene derivatives have been assigned to the $>CD_2$ group, while that at 677 cm^{-1} is due to the $>CHD$ group. In addition both groups absorb at 939 cm^{-1}.

Fluorene could be metalated readily by potassium metal using ethers such as dioxane, tetrahydrofuran or the ethers of ethylene glycol as solvents. Dialkyl ethers were inferior as solvents for the metalation, while hydrocarbons were quite inefficient. On the other hand 9-fluorenyllithium and -sodium could be prepared successfully from the metals and fluorene only in ethers of ethylene glycol or tetrahydrofuran.

The reaction of equimolar quantities of 9-fluorenylpotassium or -sodium and alkyl halides or deuterium oxide yielded mixtures of unchanged fluorene and C_9-mono and C_9-disubstituted fluorene. The amount of disubstitution was as

high as 35 per cent in ether solvents and less than 10 per cent in hydrocarbon solvents. 9-Fluorenyllithium produced exclusively monosubstituted fluorene in hydrocarbon solvents and little disubstitution in ether solvents.

A hydrogen-deuterium exchange occurred between fluorene and KOD, or KOH and D_2O, in dioxane and dimethoxyethane. No such exchange was observed with LiOD.

The reaction of benzoyl chloride with 9-fluorenylpotassium or -sodium in ether or hydrocarbon solvents yielded 9-1'-benzoyloxybenzylidenefluorene. 9,9-Dibenzoylfluorene and 9-1'-benzoyloxybenzylidenefluorene were obtained from the reaction of 9-fluorenyllithium with benzoyl chloride in ether medium, while uncontaminated 9,9-dibenzoylfluorene was formed from the reaction of 9-fluorenyllithium with benzoyl chloride in hydrocarbon solvents. Only unchanged 9-benzoylfluorene was obtained from alkali metal derivatives of 9-benzoylfluorene and ethyl benzoate.

The results are explained in terms of solubilities of the organometallic compound, participation of the ether solvents in the metalation reaction , the polarity of the carbon-metal bond and the acidity of the remaining hydrogen in the C_9-monosubstituted derivatives of fluorene.

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INTRODUCTION

1. The Problem

The acidity of the methylene group of fluorene is well established in the literature, but little is known about the metalation of fluorene and its 9-substituted derivatives by the alkali metals themselves.

In order to gain more information concerning these direct metalations and the behavior of the metal derivatives of fluorene toward various reagents, a study was made of the conditions under which such reactions would occur. The infrared spectra of various C_9-substituted derivatives of fluorene were investigated in order to furnish a suitable means to examine the products of the reactions of the organometallic compounds with appropriate reagents. It was hoped that this work would lead eventually to the development of convenient routes for the preparation of the pure uncontaminated metal salts of fluorene and of the C_9-mono- and disubstituted derivatives of fluorene.

2. Approach to the Problem.

The usual procedure for determining the extent of metalation reactions consists of reaction of the organometallic compound with carbon dioxide, followed by isolation of the corresponding carboxylic acids.

Since Gilman and Van Ess (1) have shown that the reaction of phenyllithium and carbon dioxide yields not only the expected benzoic acid but also benzophenone, triphenyl carbinol and lithium carbonate, it was desirable to employ, if possible, another method to convert the organometallic compounds completely into readily isolatable derivatives which could be estimated quantitatively. Alkylation of the metal derivatives by alkyl halides seemed to be a suitable reaction for this purpose.

Furthermore separation of the alkylated fluorenes from each other and from unreacted fluorene was to be accomplished by use of elution chromatography which thus would avoid losses of the product due to crystallization procedures. Such losses would lead to erroneous conclusions with respect to the metalation reaction itself. Since infrared spectroscopy would be a most suitable means for examination of the fractions obtained by chromatography, the absorption bands of the methylene group in fluorene and some characteristic bands of 9-substituted fluorene derivatives had to be determined. The literature concerning the infrared studies of fluorene and 9-alkyl fluorenes is meagre and thus a fundamental study of this aspect was made, using the deuteration technique and various known C_9-mono- and disubstituted derivatives of fluorene.

The most promising conditions for the direct metalation of fluorene were thought to be those involving an ether medium and hence various ether solvents have been

investigated extensively in this work. Results have been compared with similar reactions in hydrocarbon solvents. This produced several convenient preparations of pure alkali metal derivatives of fluorene and substituted fluorenes either as solutions or as isolatable solids.

The interesting results obtained from the deuteration of the alkali metal salts of fluorene with deuterium oxide led to a further study of the hydrogen-deuterium exchange of the acidic hydrogens of fluorene in ether solutions in the presence of alkali hydroxides.

Although only monometalation of fluorene should occur under the conditions employed, it was quite unexpected to learn that the reaction of the metal derivatives with equimolar amounts of alkyl halides yielded considerable amounts of C_9-dialkylated compounds. This interesting phenomenon was investigated in order to reveal the conditions under which such disubstitution is favored and how pure monoalkylfluorenes could be obtained from such reactions.

The preparation of 9,9-dibenzoylfluorene represented a special problem since the formation of this β-diketone is limited by the extremely facile enolization of the intermediate 9-benzoylfluorene under basic conditions. A procedure was sought and developed to overcome enolization and to prepare the pure β-diketone free from contaminating side products.

LITERATURE SURVEY

Fluorene, the hydrocarbon under investigation in the present work, had been discovered as early as 1867 by Berthelot (2). Since then it has been the subject of several hundred interesting reactions, many of which are reviewed by Rieveschl and Ray up to the period of 1938 (3).

The acidity of the methylene hydrogen atoms in fluorene and other hydrocarbons had been determined by Conant and Wheland (4). From this work the relative acidity of some of the compounds investigated were found to be :

phenylacetylene $>$ indene $>$ 9-phenylfluorene $>$ fluorene $>$ triphenylmethane. These relative acidities were determined mainly from the extent of metalation which occurred when a metal derivative of one hydrocarbon was allowed to equilibrate with another "acidic" hydrocarbon. Treatment of the equilibrium mixture with carbon dioxide yielded the carboxylic acids of the two hydrocarbons involved. Assuming the carbonization to be complete and faster than crossmetalation, the relative amounts of carboxylic acids isolated were taken as diagnostic for the position of the equilibrium of the metalation reaction.
The relative acidity scale is based on acetophenone which had been assigned arbitrarily a value of pK = 20 since it was found to be a slightly weaker acid than is ethyl alcohol with the known dissociation constant $K = 7 \times 10^{-20}$.

McEwen (5) extended this series to other hydrocarbons and to amines and alcohols, using colorimetric, spectrophotometric and polarimetric methods for the evaluation of the intermetalation equilibrium. Thus fluorene was assigned a pK of 25, which places it between 9-phenylfluorene and indene, both of which have a pK of 21, and triphenylmethane and diphenylmethane with a pK of 33 and 35 respectively. This appears to be reasonable on theoretical grounds. Due to the active methylene group fluorene and its 2-, and 2,7-substituted derivatives have been successfully condensed with aromatic aldehydes (6 - 11) in the presence of strong bases to yield products, such as 9-benzylidenefluorene, a product obtained from the reaction of benzaldehyde and fluorene. Condensations of fluorene and aliphatic aldehydes and ketones (12, 13), though more difficult to bring about, were satisfactorily achieved in a few cases (10, 14).

The information concerning the infrared studies of fluorene and its 9-substituted derivatives is meagre. Fox and Martin (15) in a study of the absorption in the 3000 cm^{-1} region attributed two frequencies, 2901 cm^{-1} and 2795 cm^{-1}, to the methylene group of fluorene. Richards and Thompson (16), investigating the spectral changes occurring in liquid-solid state transitions, found two frequencies 1303 cm^{-1} and 1482 cm^{-1}, apparently characteristic of fluorene.

Examination of the literature has shown that up to the present time no thorough investigation of the direct metalation of fluorene by alkali metals has been made. There are reports of attempts at metalation of fluorene using various reagents. Weissgerber (17, 18) treated molten fluorene with potassium hydroxide and sodamide at temperatures between 150° and 200° C, but these procedures were found to be unsatisfactory (19). Greenhow (19) reported considerably better results using sodamide in boiling decahydronaphthalene to bring about metalation of fluorene. Schlenk and Bergmann (20) prepared 9-fluorenylsodium by the reaction of triphenylmethylsodium with fluorene. However, the presence of triphenylmethane complicated the isolation and purification of the reaction products. Morton (21) reported the preparation of metal derivatives of fluorene by crossmetalation using the intermediates made "in situ" from alkali metals and alkyl or aryl halides. The work of Hückel (22) indicated that sodium metal does not substitute for hydrogen but instead adds to fluorene when the reaction is carried out in liquid ammonia.

Gilman and Gorsich (23) have reported that lithium does react directly with fluorene and with cyclopentadiene in tetrahydrofuran to form 9-fluorenyllithium and cyclopentadienyllithium respectively. Recently a paper by Normant and Angelo (24) described the metalation of a number of hydrocarbons, primarily with sodium, but in some examples with lithium or potassium, using as the intermediate metalating agent the product

arising from the combination of the metal with naphthalene. The mixture of naphthalene, tetrahydrofuran, metal and active hydrogen compound gave metalation of a number of hydrocarbons, which previously had reacted very slowly of failed to react at all with metallic sodium. The use of amines or of special ethers such as dimethyl ether and 1,2-dimethoxyethane to facilitate the addition of alkali metals to hydrocarbons such as naphthalene, biphenyl, etc., and the utility of these addition compounds to prepare alkali metal salts of active hydrogen-containing hydrocarbons had been pointed out previously by Scott et al. (25). However, the prensence of naphthalene and the dihydronaphthalene byproduct complicated isolation and purification of the reaction products.

There are some reports in the literature that disubstitution rather than the expected monosubstitution occurred in reactions involving the reaction of alkali metal derivatives of organic compounds with such compounds as alkyl halides. But in all these cases there was either a strongly activating group attached to the compound under investigation which caused a particular hydrogen atom to attain enhanced acidity, or the molar amounts of reagents employed were such as to favor disubstitution. The former concept was used to explain the results of Hauser (26), who obtained a mixture of disubstituted, monosubstituted and unreacted product from the reactions of benzyl chloride and the monopotassium salt of

dibenzylketone or dibenzylsulfone. The excess of reagents used no doubt caused the disubstitution which was found unknowingly by Weissgerber (18) and reported by Thiele and Henle (7) as occurring upon treatment of fluorene with benzyl chloride in the presence of sodium amide. Another instance of the effect of the use of excess reagents is the disubstitution observed by King et al. (27) from the reaction of fluorene with acrylonitrile. No doubt, for the same reason Seibert and Bergstrom (28) obtained some diphenylfluorene from the reaction of fluorene, potassium amide and bromobenzene. However, King (27) also reported that equivalent amounts of acrylonitrile and indene produced a disubstituted indene derivative. In addition, from the investigation of the alkali metal derivatives of acetonitrile and phenylacetonitrile in liquid ammonia and their reactions with alkyl halides Hauser and Brasen (29), Bergstrom and Agostinho (30) and Schuerch and Huntress (31) reported the occurrence of disubstitution. No disubstitution occurring upon alkylation of fluorene using equimolar amounts of reagents has been observed hitherto. However, the cases cited above suggest that this phenomenon might occur when the monometal salt of fluorene is treated with an equivalent amount of organic halide.

The reaction of the acid halide, benzoyl chloride, with an equivalent amount of the monometal salt of fluorene produces 9,9-dibenzoylfluorene or 9-1'-benzoyloxybenzylidenefluorene depending upon the conditions of the reaction. The first preparation of 9,9-dibenzoylfluorene was recorded by Schlenk and Bergmann (32, 33) who, from the reaction between 9-fluorenyllithium and

benzoyl chloride in benzene, isolated di-(9-fluorenyl)-phenylcarbinol along with a compound of unknown structure melting at 180° C. This compound, obtained only by painstaking effort, was later identified by Kliegl et al (34) as the 9,9-dibenzoylfluorene. Subsequent preparations of the diketone have followed this (35) or similar procedures (27). However the reaction of benzoyl chloride with 9-fluorenylsodium in ether produced 9-1'-benzoyloxybenzylidenefluorene as was first shown by Kliegl and coworkers (34). In this connection can be cited the work of King, Meltzer and Doczi (27) who prepared 9-propionylfluorene by the reaction of 9-fluorenyllithium with propionyl chloride in ether at reflux temperature. At room temperature conditions 9,9-dipropionylfluorene was obtained.

The 9-benzoylfluorene has been synthesized by Werner and Schöler (36) and Wislicenus and Fehrle (37) from the reaction of fluorene with potassium metal and ethyl benzoate.

No preparative method has yet been advanced for the synthesis of 9,9-dibenzoylfluorene.

RESULTS AND DISCUSSIONS

1. The Infrared Spectra of Fluorene and its 9-Substituted Derivatives.

In this thesis are reported the infrared spectra of fluorene and the following C_9-substituted derivatives: Mono- and dideuterofluorene, mono- and dimethylfluorene, mono- and diethylfluorene, mono- and dibenzylfluorene, mono- and diallylfluorene as well as 9-benzylidenefluorene and fluorenone. Also the spectra of 9-deutero-9-methylfluorene and 9-deutero-9-benzylfluorene are shown for comparison. These spectra were obtained using both carbon disulphide and carbon tetrachloride solutions to provide the whole range of absorption from 4000 to 600 cm^{-1}, except for a small region about 1450 to 1600 cm^{-1}, where both solvents show some absorption themselves (38).

The spectra, taken in carbon tetrachloride solution with a Perkin Elmer model 21 double beam spectrophotometer equipped with a sodium chloride prism, did not reveal clearly the absorption at the two frequencies 2901 cm^{-1} and 2795 cm^{-1}, reported by Fox and Martin (15) to be due to the methylene group of fluorene. However, spectra taken at a later stage of this work with a Perkin Elmer model 221 spectrophotometer, giving better resolution in the C-H stretching region, not only confirmed the presence of those two bands but proved them to be associated with the methylene group since they were eliminated

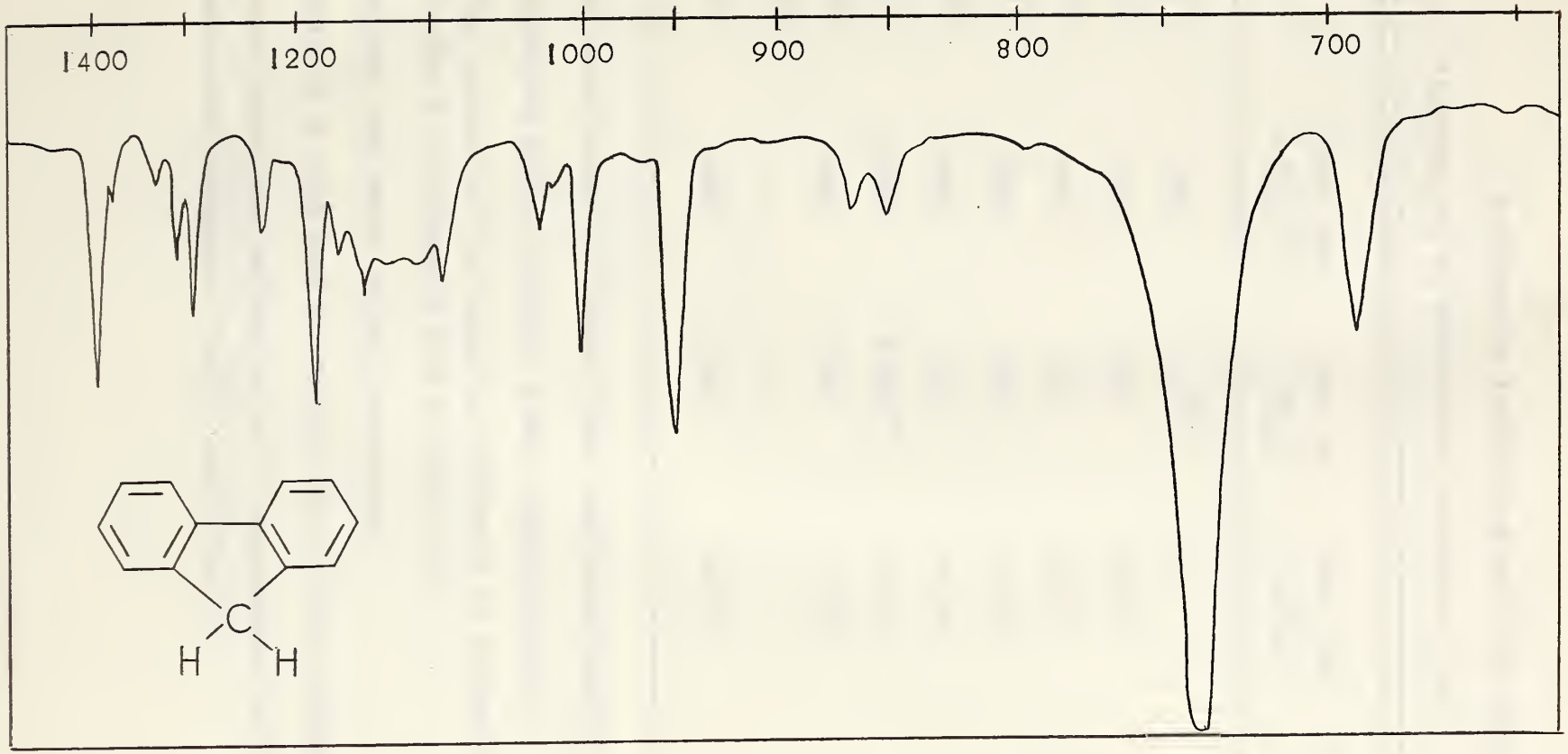
in the spectrum of deuterated fluorene. The two absorption bands at 1303 cm^{-1} and 1482 cm^{-1}, reported by Richards and Thompson (16) as apparently characteristic of fluorene, were confirmed in this work. However, the deuteration experiments revealed that only the 1300 cm^{-1} band is definitely associated with the methylene group while the 1482 cm^{-1} band appears to be due to some other vibrations of the fluorene structure.

During the course of studies with the Perkin Elmer model 21 spectrophotometer six frequencies of medium intensity were found definitely due to the methylene group of fluorene. These are at 2930, 1400, 1298, 1190, 952 and 692 cm^{-1} (FIG. 1). Whether these are all fundamental frequencies or not is not known. There are, no doubt, other frequencies due to the methylene group arising from overtones and combinations, but these were felt to be unnecessary for the present work, because their low intensity make them of little assistance in identifying fluorene in mixtures of substituted fluorenes. Two such frequencies of low intensity are believed to be at 867 cm^{-1} and 853 cm^{-1} (Fig. 1).

All six frequencies can be clearly discerned and are of approximately the same intensity in both solvents employed. Since additional frequencies associated with substituting groups appear in the 1400 cm^{-1} to 600 cm^{-1} region, this area was

examined carefully and thus only the spectra for this region, found in carbon disulphide, are reported and shown in Figures 1 to 16. Each of the six frequencies mentioned is markedly affected by substitution or deuteration at C_9. In all cases monosubstitution by alkyl or aralkyl groups greatly reduces or eliminates the absorption at these frequencies, while disubstitution removes it completely. The removal of some is masked by neighboring frequencies or new absorption bands due to the substituting groups but can still be readily observed. Mono- and dideuteration reduces or removes these bands similarly, but new bands appear for the C-D functions at lower frequencies as expected (Figs. 2 and 3).

The relative position of the new C-D absorption frequency of each C-H band was estimated beforehand from Fig.1, using the suggested factor of 0.73 (38), and thus the new frequencies could be related at least tentatively, if not exactly, to the former C-H frequencies. The experimentally found ratio of the new C-D frequency to the original C-H frequency is approximately 0.70 to 0.76 and agrees well with that generally accepted (38). The frequencies for the original CH_2 bands, the new C-D bands of the dideuterated molecule and the CHD bands of the monodeuterated molecule, as well as the ratio of the first two, both found and calculated, are shown in Table I .



F i g . 1 Partial infrared spectrum of fluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

Table I

Frequencies Associated with the Methylene Group in Fluorene and in Deuterated Fluorenes (cm^{-1})

Obs. for $-CH_2-$	Calc. for $-CD_2-$ [c]	Obs. for $-CD_2-$	Obs. for C-D/C-H	Obs. for -CHD-
692 [a]	505	-- [d]	--	677
952 [a]	694	667	0.70	939
1100 [a]	869	827	0.70	-- [f]
1298 [a]	947	939	0.72	-- [f]
1400 [a]	1022	974	0.70	-- [f]
2930 [a]	2050	2150 [e]	0.73	-- [f]
2901 [b]	2120	2190	0.755	2175
2795 [b]	--	--	--	--
2885 [b]	2100	2120	0.733	

(a) Spectrum taken on Perkin Elmer spectrophotometer model 21.

(b) Spectrum taken on Perkin Elmer spectrophotometer model 221.

(c) The product of the observed frequency in column 1 and the factor 0.73 obtained from reference 38.

(d) Beyond the range of the instrument.

(e) This is a very weak absorption and is not certain.

(f) Overlapping and multiplicity of neighboring absorption makes any assignment highly questionable.

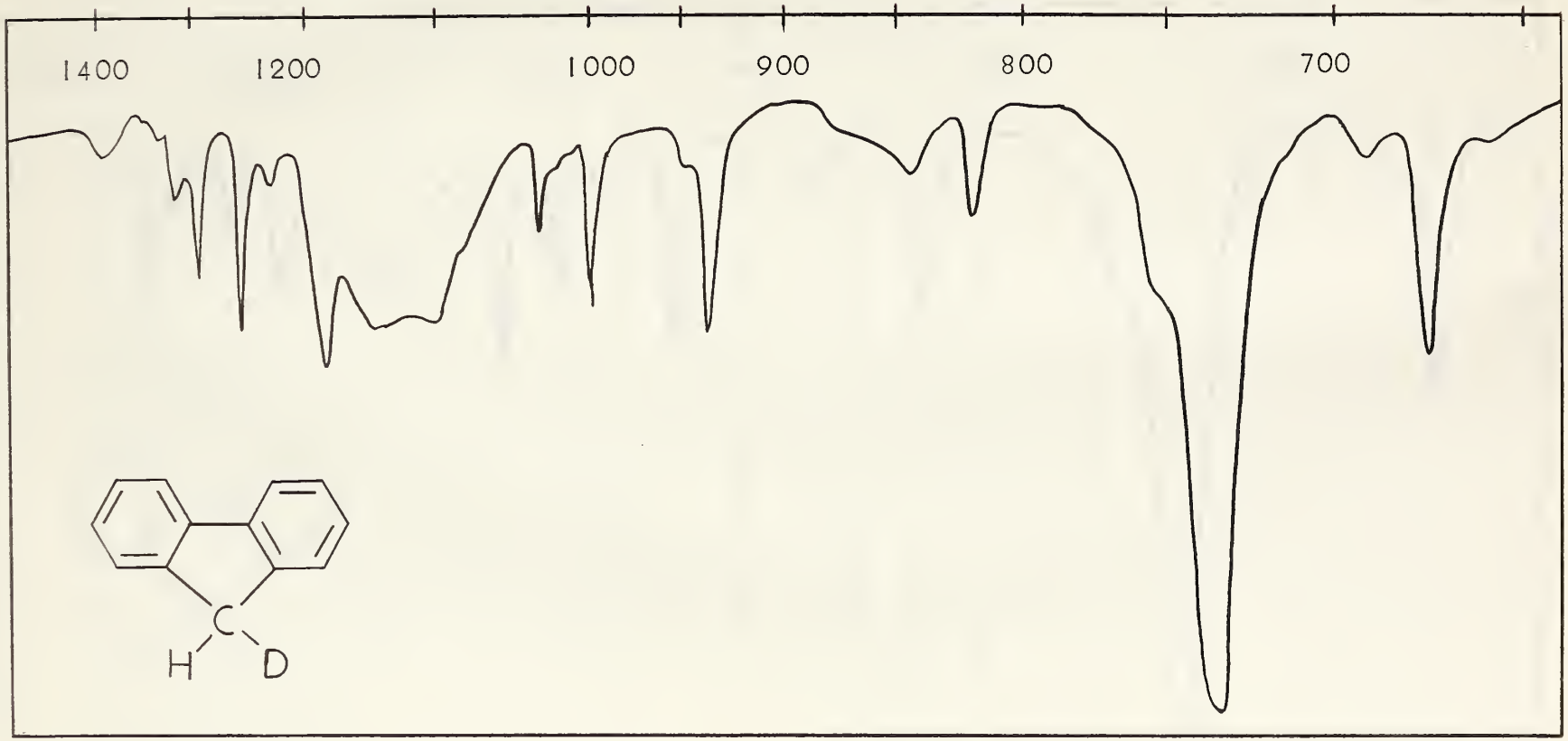


Fig. 2. Partial infrared spectrum of 9-deuterofluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

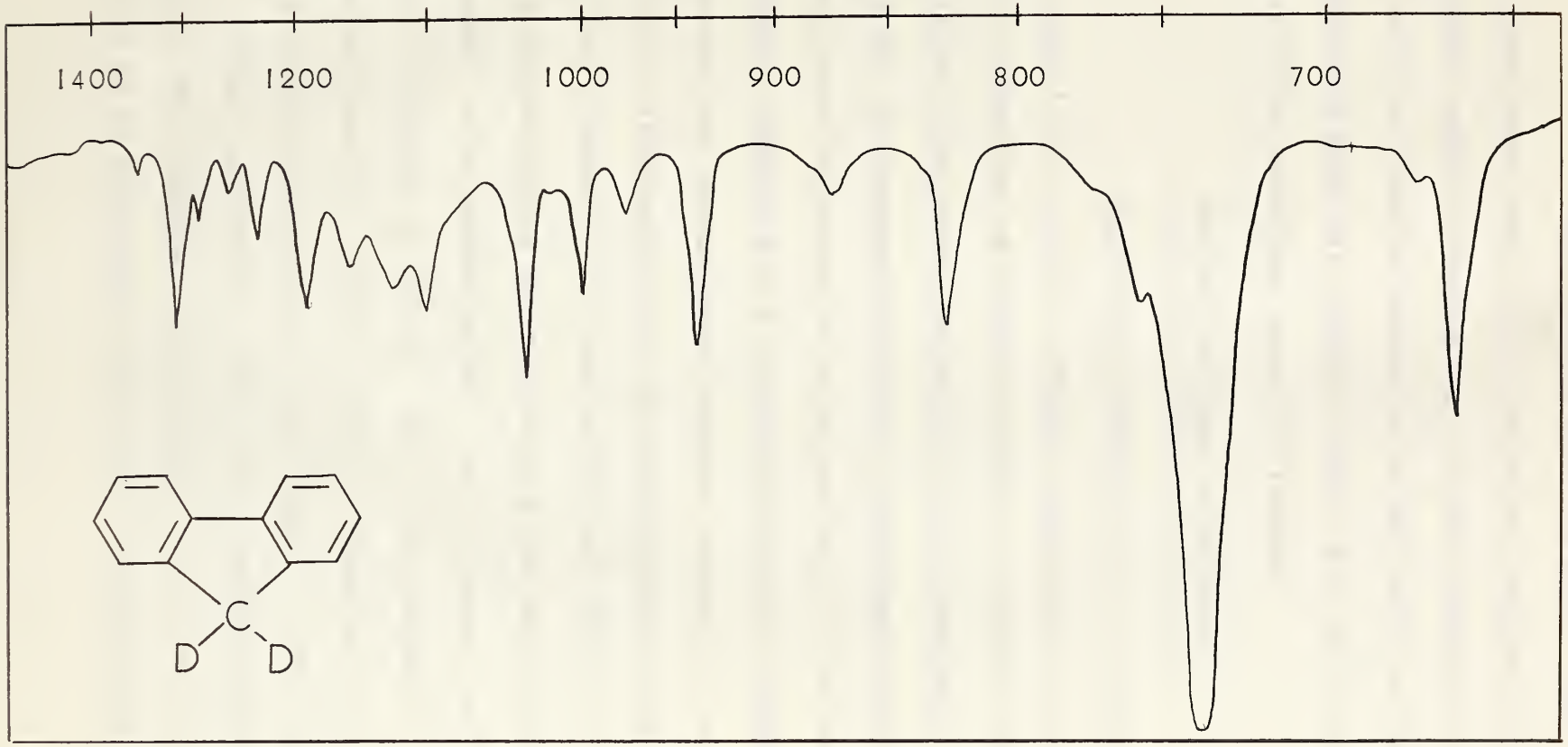


Fig. 3 Partial infrared spectrum of 9,9-dideuterofluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

Later studies with the Perkin Elmer spectrophotometer model 221, with better resolution in the C-H stretching region, revealed that the band previously found at 2930 cm^{-1}, is a doublet occurring at 2901 cm^{-1} and 2885 cm^{-1}. In addition a weak but distinct band at 2795 cm^{-1} could be related to the methylene group of fluorene.

The 692 cm^{-1} Band of Fluorene.

This band, probably due to methylene rocking vibrations (38), is quite distinct. Monodeuteration via the lithium derivative of fluorene reduces it markedly (Fig. 2). The residual absorption noticeable at this frequency is most likely due to unreacted fluorene, a contaminant undoubtedly present since the deuterium oxide available at the time of these experiments contained 95 % D_2O. Purification by separation of deuterated from undeuterated fluorene obviously is extremely difficult. Dideuteration via the "dipotassium fluorenyl" completely eliminates the band at 692 cm^{-1} (Fig.3). The spectrum of the monodeuterated fluorene shows a new band at 677 cm^{-1}, which is thought to be associated with the CHD group, shifted from the original frequency of 692 cm^{-1} due to the presence of the deuterium atom. This point of view is supported by the fact that dideuteration reduces this 677 cm^{-1} band to a very small value, this residual absorption arising from contaminating monodeuterated fluorene. The frequency corresponding to the new $>CD_2$ group, calculated to be in the region of 505 cm^{-1}, is beyond the range studied.

Monomethylation reduces the band at 692 cm^{-1} to one of weak absorption at the same frequency (Fig.4). This was found to be due to contamination by unreacted fluorene since repeated purification by chromatography on activated alumina eliminated the absorption at 692 cm^{-1} (Fig.5). The disappearance of the 692 cm^{-1} band on monobenzylation and dibenzylation is masked by the strong absorption at 697 cm^{-1} due to the C-H out-of-plane deformation vibrations of monosubstituted benzene (38) (Figs. 10 and 12).

Mono- and diallylation (Figs. 13 and 14) show more clearly the disappearance of the 692 cm^{-1} band. The spectrum of fluorenone (Fig.16) also shows clearly the absence of any absorption at this frequency. The expected complete elimination of the 692 cm^{-1} band in 9-benzylidenefluorene (Fig.15) is obscured by the strong absorption at 697 cm^{-1} due to monosubstituted benzene.

The 952 cm^{-1} Band of Fluorene.

This band, whose origin is unknown, is also quite distinct (Fig.1). It is nearly eliminated by monodeuteration , the residual absorption most likely being due to contaminating fluorene (Fig.2). Dideuteration causes complete disappearance of absorption at this frequency. The corresponding $>CD_2$ band, calculated to occur in the region of 694 cm^{-1}, appears at 667 cm^{-1} with comparative intensity as

shown in the spectrum of dideuterated fluorene (Fig.3).

The band due to the >CHD group, if analogous to that of 677 cm^{-1} found for the 692 cm^{-1} band, should occur in the region of 935 cm^{-1} . One actually does appear at 939 cm^{-1} and may contain this type of absorption. However, the magnitude of its intensity as well as the fact that dideuteration makes no significant changes in its size favors the view that two different types of vibration absorb at 939 cm^{-1}. These are thought to be the methylene absorption, originally at 1298 cm^{-1}, shifted due to the substitution of both of its hydrogen atoms by deuterium, and the absorption from the >CHD group shifted from 952 cm^{-1} due to the presence of one deuterium atom.

The monomethyl-, monobenzyl-,and monoallyl-fluorene (Figs. 4, 5, 10, 13) all show very strong reduction of intensity or complete elimination at 952 cm^{-1}, any residual absorption again being due to contamination by unreacted fluorene.

As expected, 9-benzylidenefluorene shows no absorption in the 950 - 956 cm^{-1} region (Fig.15). A similar result occurs for the other 9,9-disubstituted fluorenes (Figs. 7, 12, 14). The position of the absorption for the C-H bond in the monosubstituted fluorenes is determined by deuteration. Comparison of the spectra of 9-methylfluorene and 9-deutero-9-methylfluorene (Figs.5 and 6) show that two bands, 692 and 722 cm^{-1}, are

eliminated on deuteration, hence it is likely that these are due to the C_9-H bond in 9-methylfluorene. Whether one of these corresponds to the absorption of the methylene group at 952 cm^{-1} cannot be decided. Similarly, the bands at 787 cm^{-1} (weak) and 719 cm^{-1} (strong) in the spectrum of 9-benzylfluorene (Figs. 10 and 11), and those at 789 cm^{-1} (weak) and 727 cm^{-1}(strong) in the 9-allylfluorene (Fig. 13) are likewise to be associated with the remaining C_9-H bond, since deuteration or disubstitution eliminates the absorption.

In addition it might be pointed out that the bands at 1100, 1167 and 1185 cm^{-1} are eliminated upon deuteration of the monomethylfluorene (Figs. 5 and 6), hence they may also be considered as associated with the remaining C_9-H bond.

The 1190 cm^{-1} Band of Fluorene.

The cause of the absorption at this frequency is not known. It was at first believed to be composed of absorption due to the methylene group and to some extent to some other structural feature since monodeuteration reduces it to about one-half its former intensity while dideuteration produces little further change. (Figs. 1 - 3). However, monosubstitution reduces the band markedly while disubstitution practically removes it, hence the absorption seen at 1190 cm^{-1} in the dideuterated molecule may be due to shifts, or combinations of overtones, stemming from deuteration at C_9. The frequency of the

The frequency of the $>CD_2$ group, expected around 869 cm^{-1}, appears at 827 cm^{-1} in fair agreement with the calculated value. The position of the absorption of the $>CHD$ group as effected by the presence of the deuterium atom could not be defined in view of the complexity of the neighboring bands.

The 1298 cm^{-1} Band of Fluorene.

This absorption is probably due to the methylene wagging vibration which, in agreement with previous observations (38), is of lower intensity than that from the rocking vibration. The band is reduced on monodeuteration or monosubstitution at C_9, while dideuteration or disubstitution largely eliminates it. Neighboring absorption bands mask these effects somewhat with the result that this frequency is less useful than are the others mentioned above.The $>CD_2$ frequency appears at 939 cm^{-1} in the dideuterated molecule. Since its intensity is practically the same in mono- and dideuterated fluorene, the view is supported that two types of absorption occur here - the monodeuterated structure, shifted slightly from 952 cm^{-1}, and the dideuterated structure, shifted from 1298 cm^{-1}.

The 1400 cm^{-1} Band of Fluorene.

This absorption is quite likely derived from scissoring vibration of the methylene group (38), since any type of mono- or disubstitution at C_9 eliminated this band.

The absorption band attributed to the new $>CD_2$ group obtained on dideuteration might be that appearing at 974 cm^{-1}. This agrees quite well with the calculated value (Table I).

The band at 1038 cm^{-1} appearing on dideuteration agrees roughly with the calculated shift, but examination of the spectra of mono- and disubstituted compounds (Figs. 4 - 16) shows that any mono- or disubstitution gives rise to a band, increasing upon disubstitution, at about the same frequency. Hence the absorption at 1038 cm^{-1} certainly cannot be due to the $>CD_2$ group.

The 2930 cm^{-1} Band of Fluorene.

Absorption in this region was studied in carbon tetrachloride solution. The spectrum taken with the Perkin Elmer model 21 showed absorption at about 2930 cm^{-1}, arising from the C-H stretching vibration. It must be due to the methylene group since it is markedly reduced upon deuteration (Figs. 19 and 20), but no firm assignment could be made for the absorption of the C-D stretching vibration. A weak absorption appears at 2150 cm^{-1} in the deuterated molecule. This shift is in agreement with the calculated shift, Table I, but the absorption is rather weak.

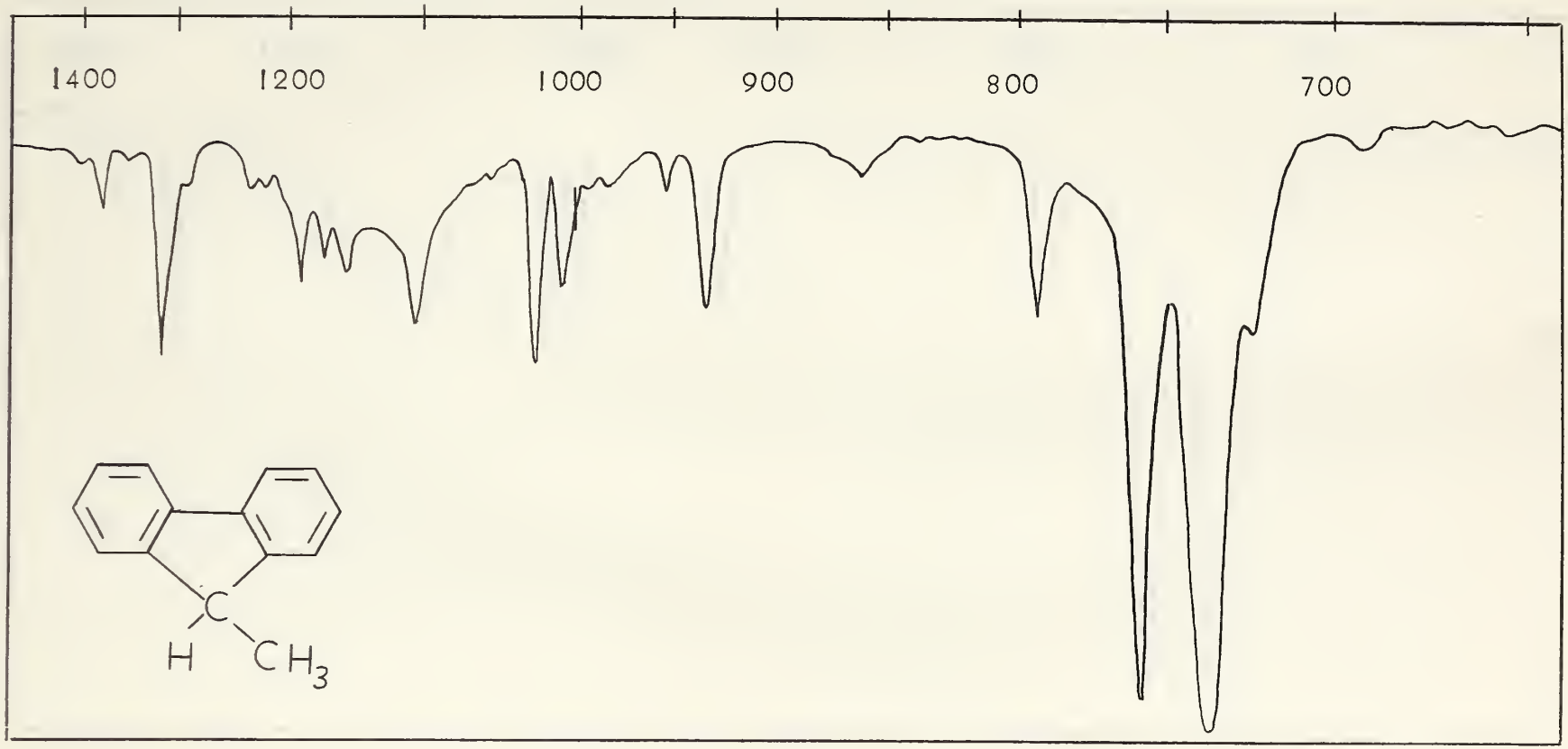


Fig. 4 Partial infrared spectrum of 9-methylfluorene (contaminated by some fluorene) in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

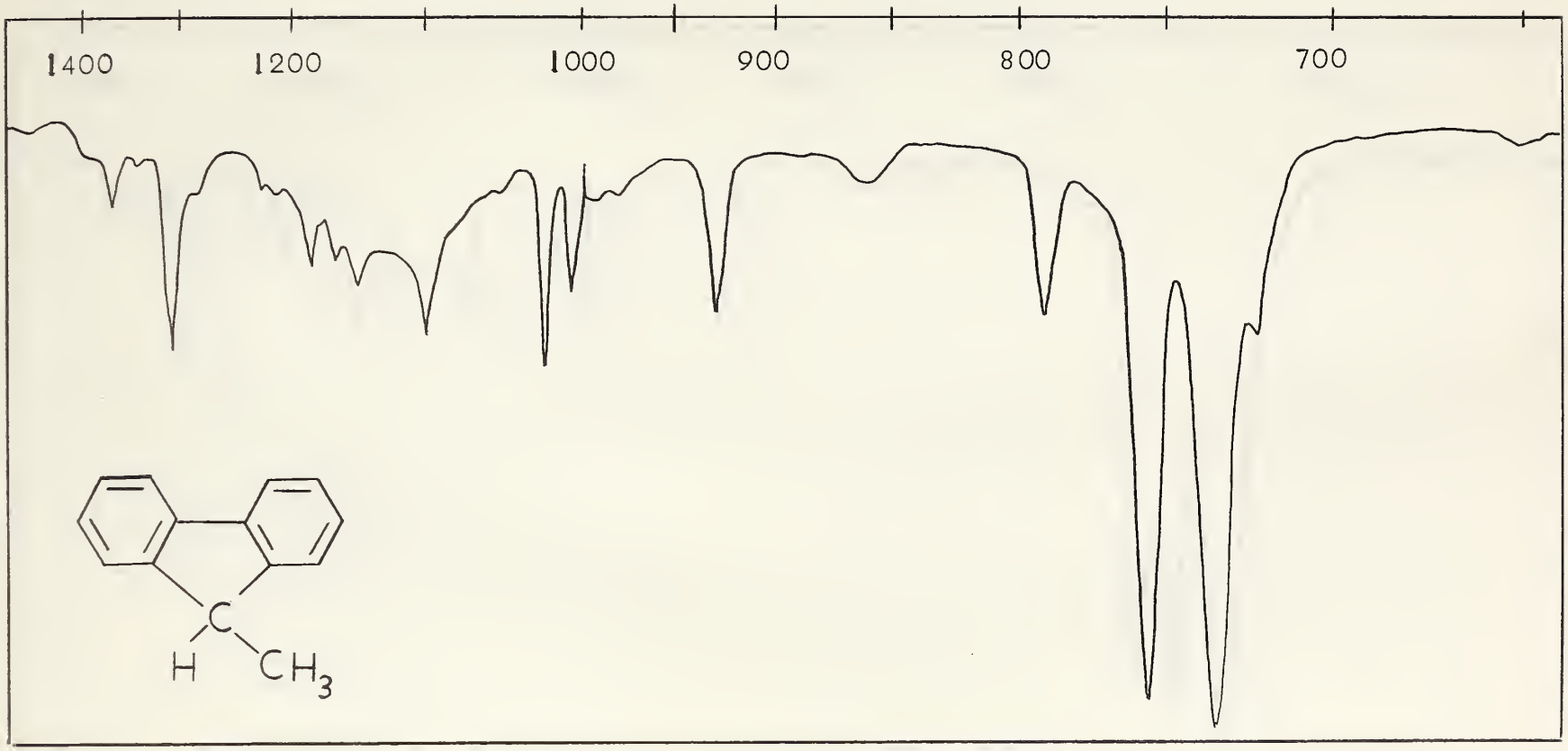


Fig. 5 Partial infrared spectrum of 9-methylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

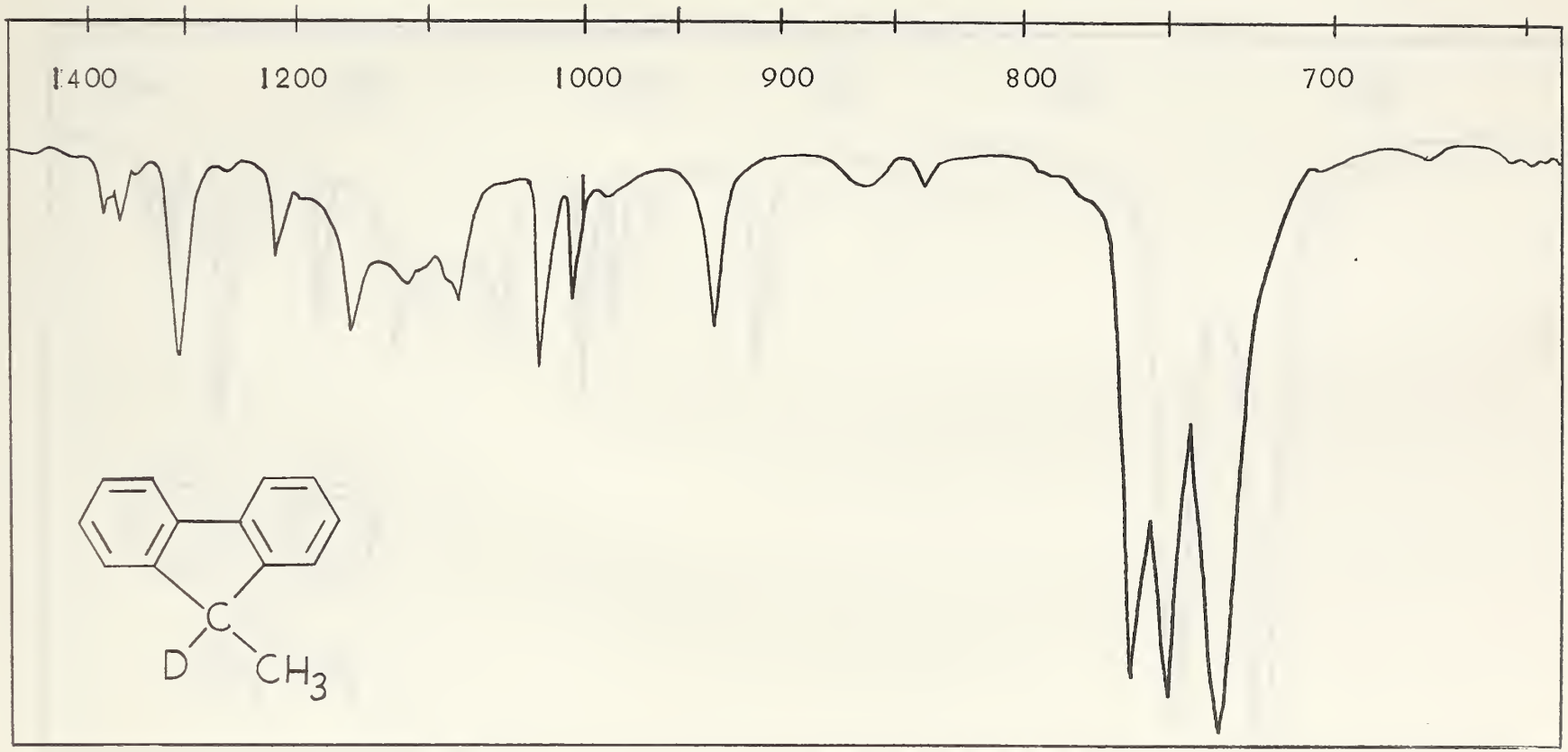


Fig. 6 Partial infrared spectrum of 9-methyl-9-deuterofluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

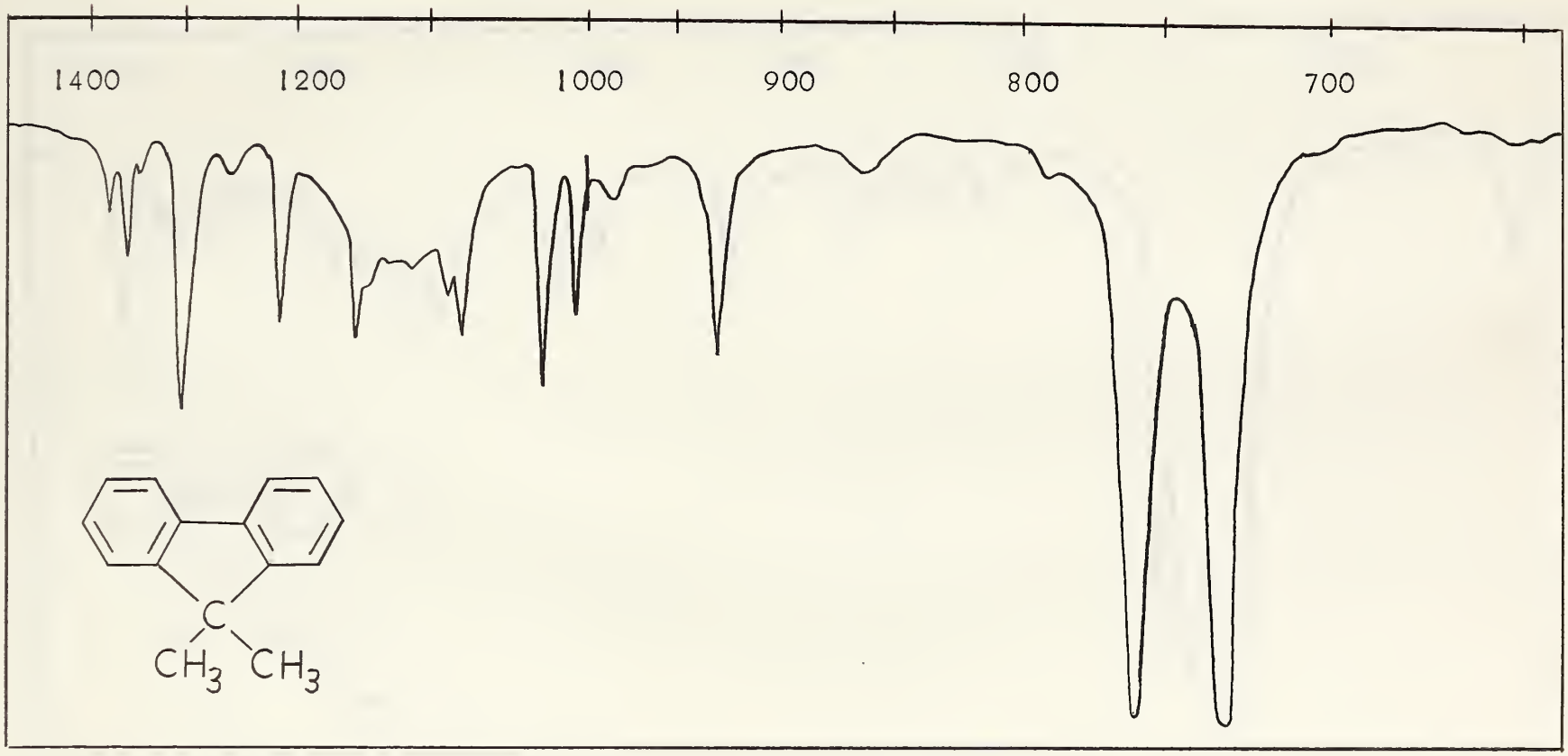


Fig. 7 Partial infrared spectrum of 9,9-dimethylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

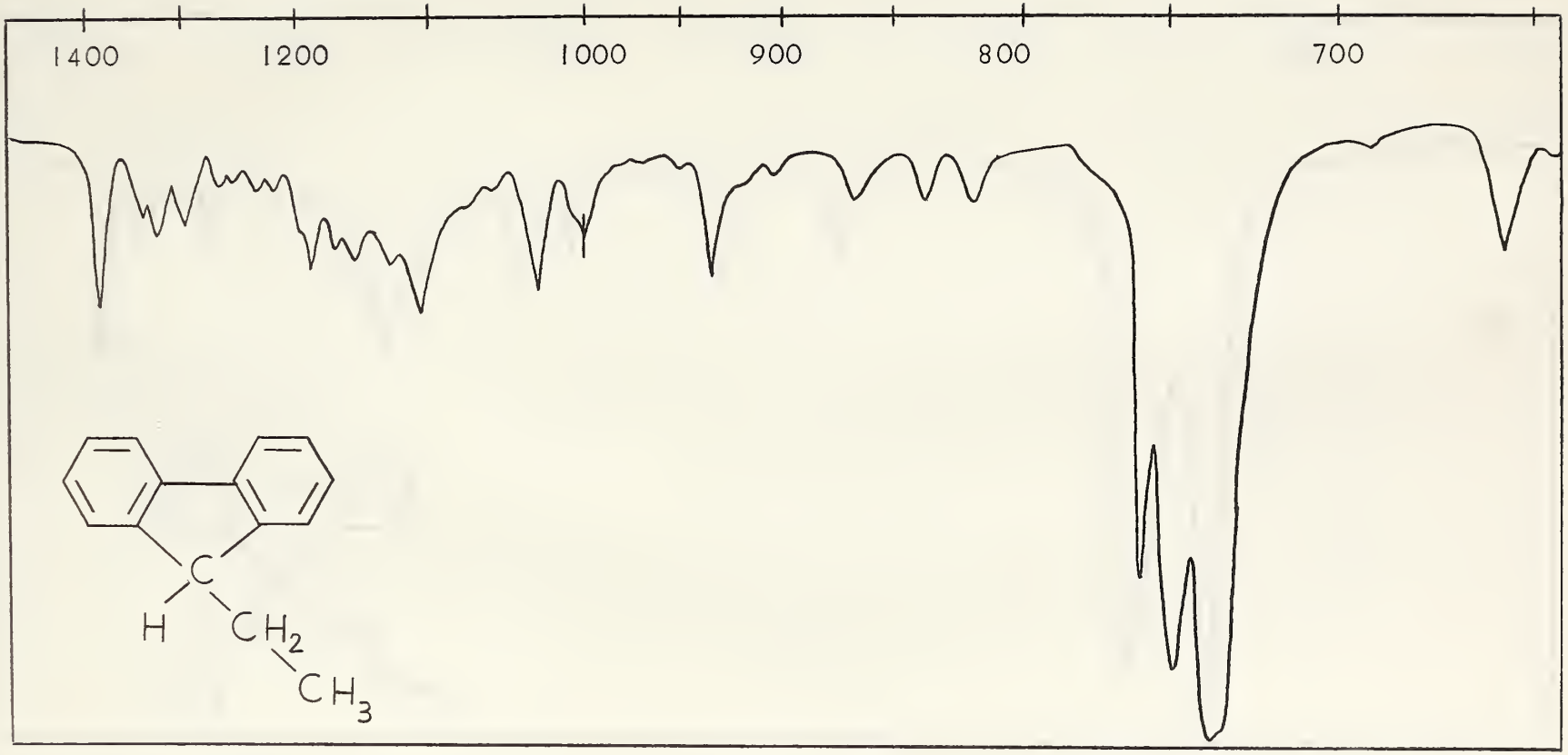


Fig. 8 Partial infrared spectrum of 9-ethylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

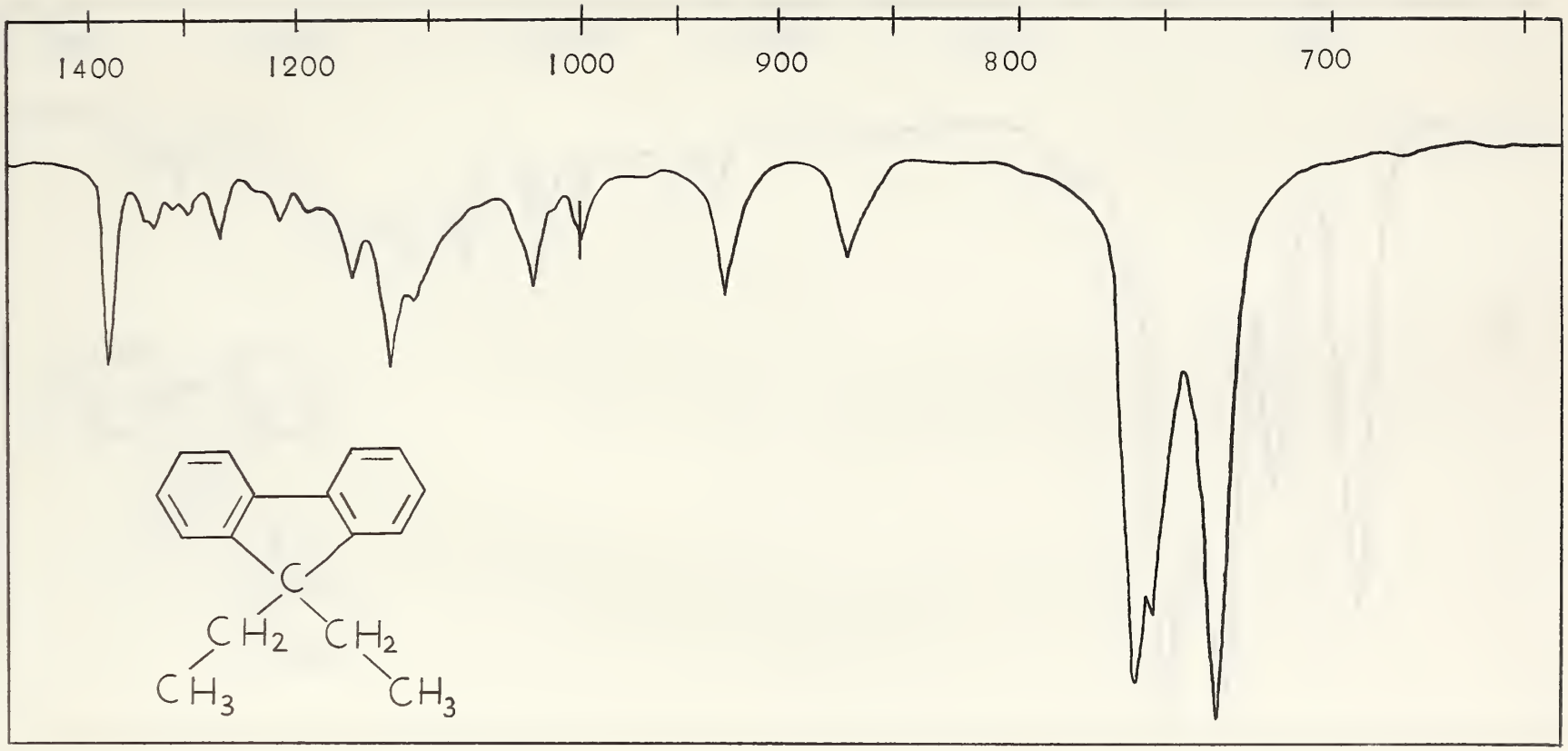


Fig. 9 Partial infrared spectrum of 9,9-diethylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

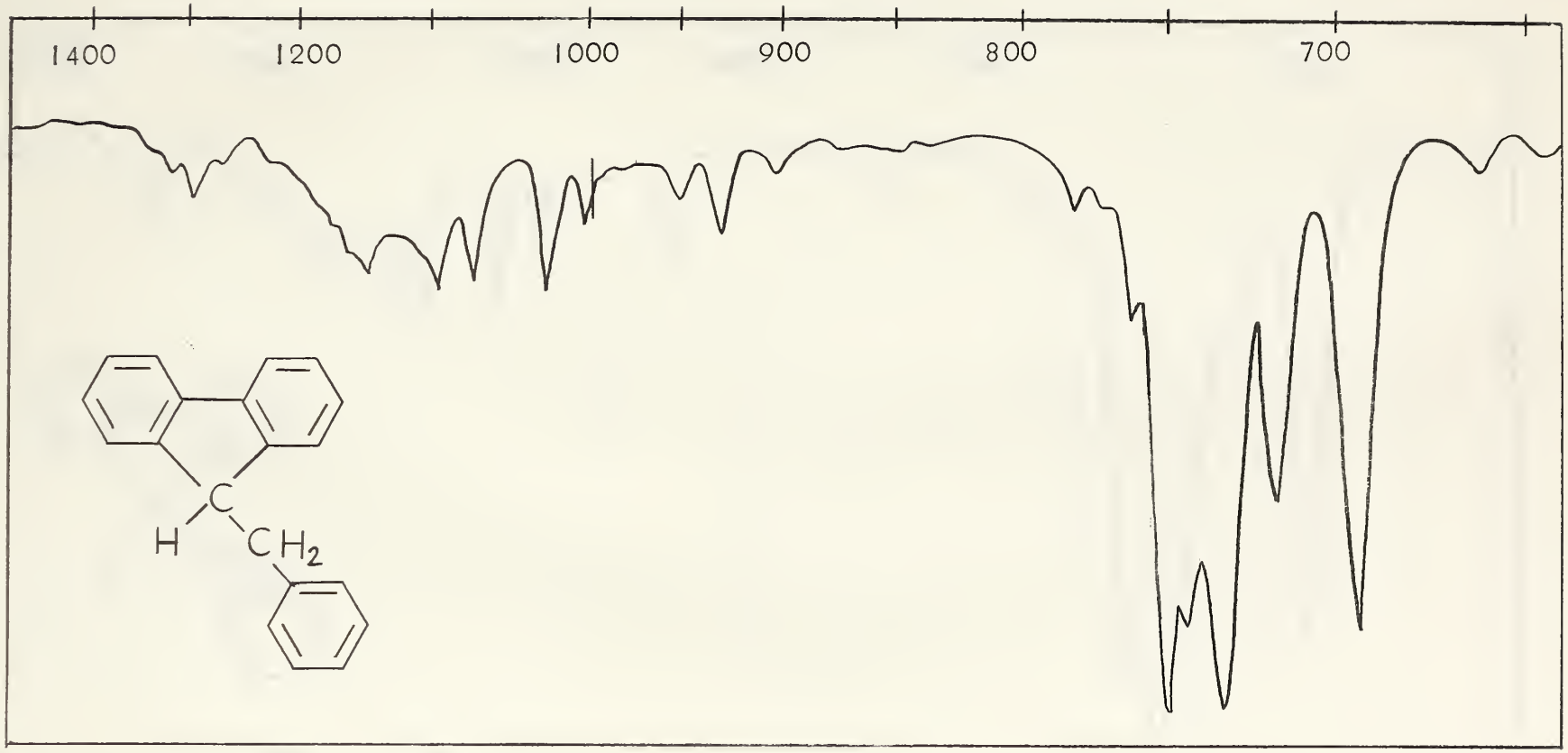


Fig. 10 Partial infrared-spectrum of 9-benzylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

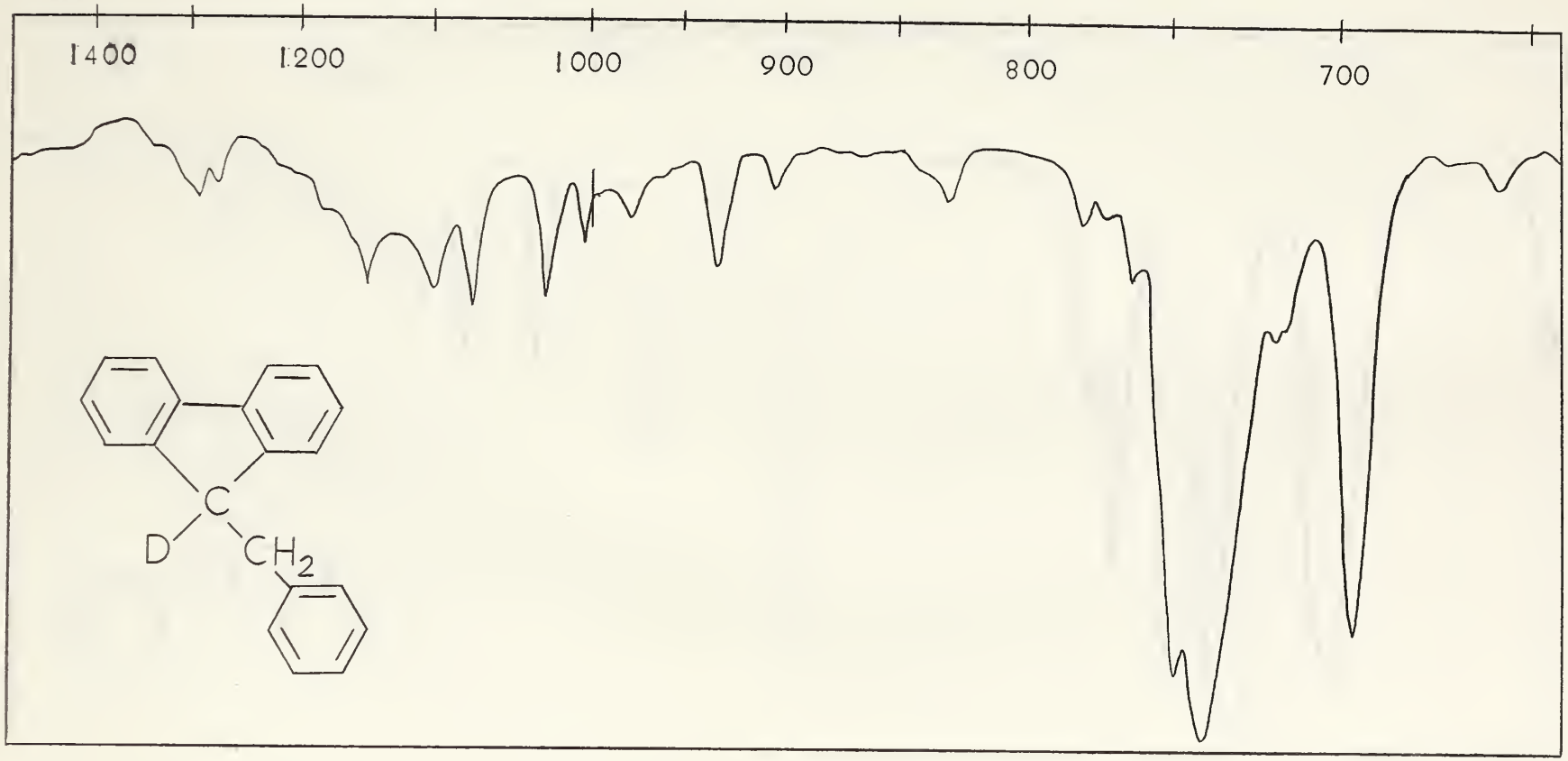


Fig. 11 Partial infrared spectrum of 9-benzyl-9-deuterofluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

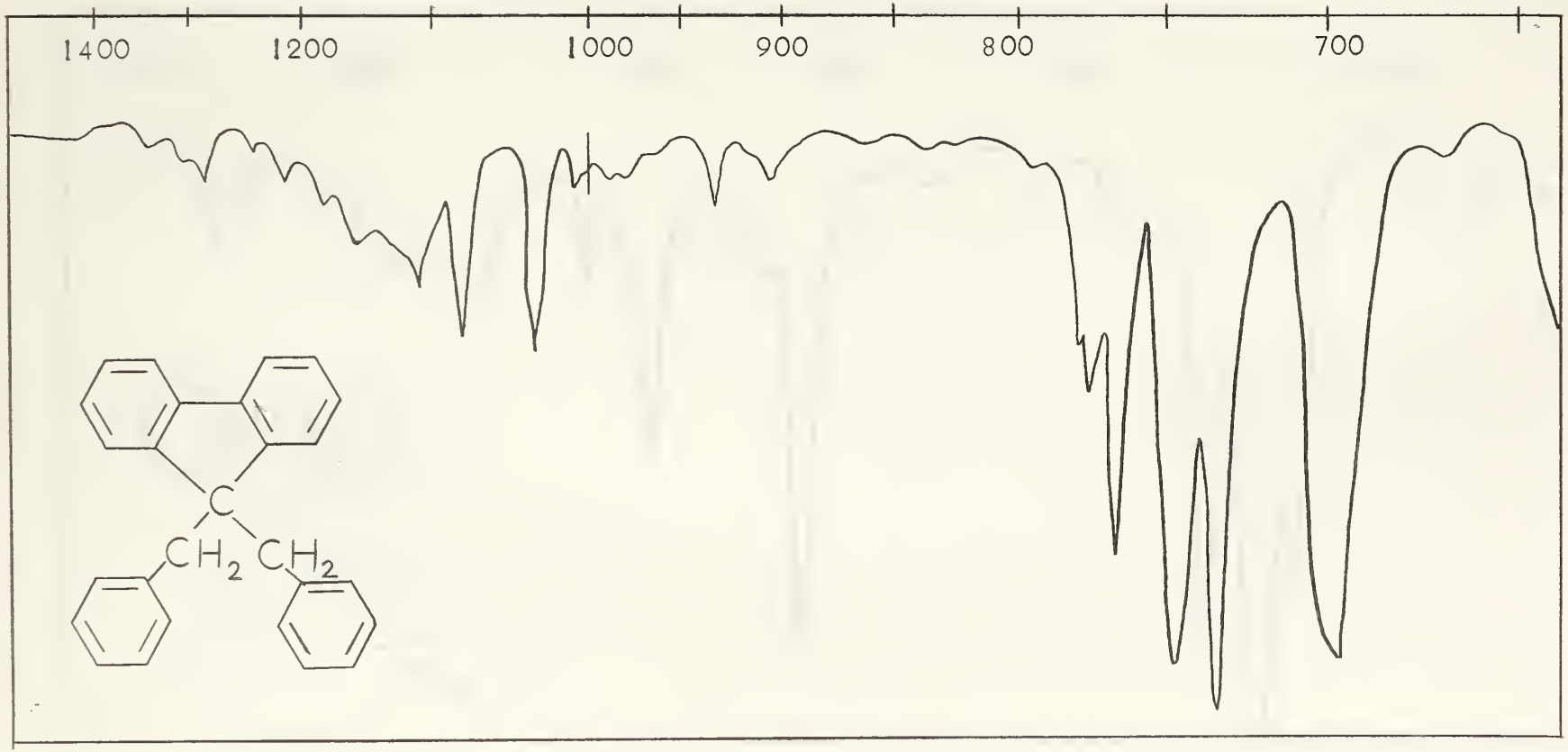


Fig. 12 Partial infrared spectrum of 9,9-dibenzylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

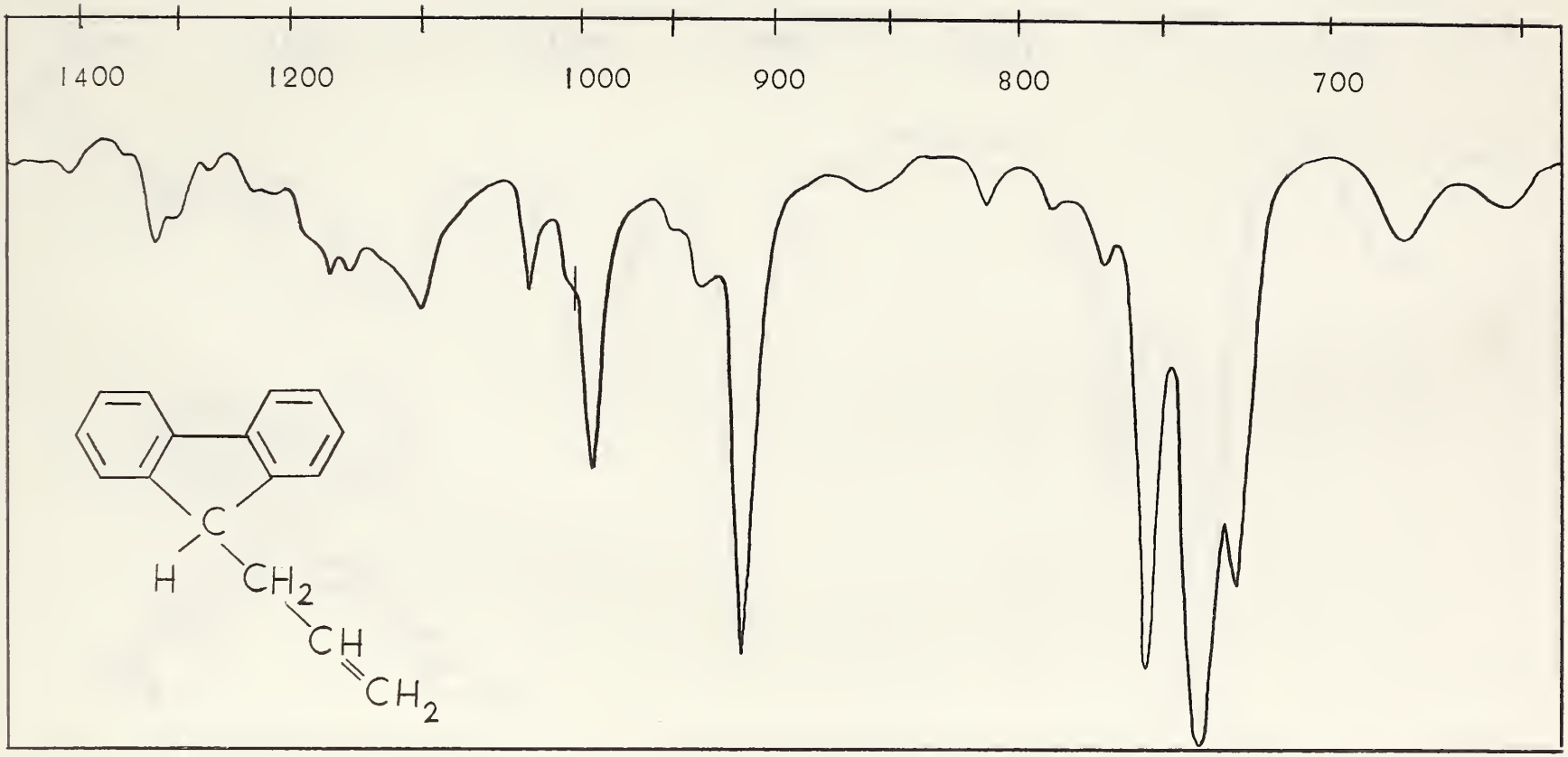


Fig. 13 Partial infrared spectrum of 9-allylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

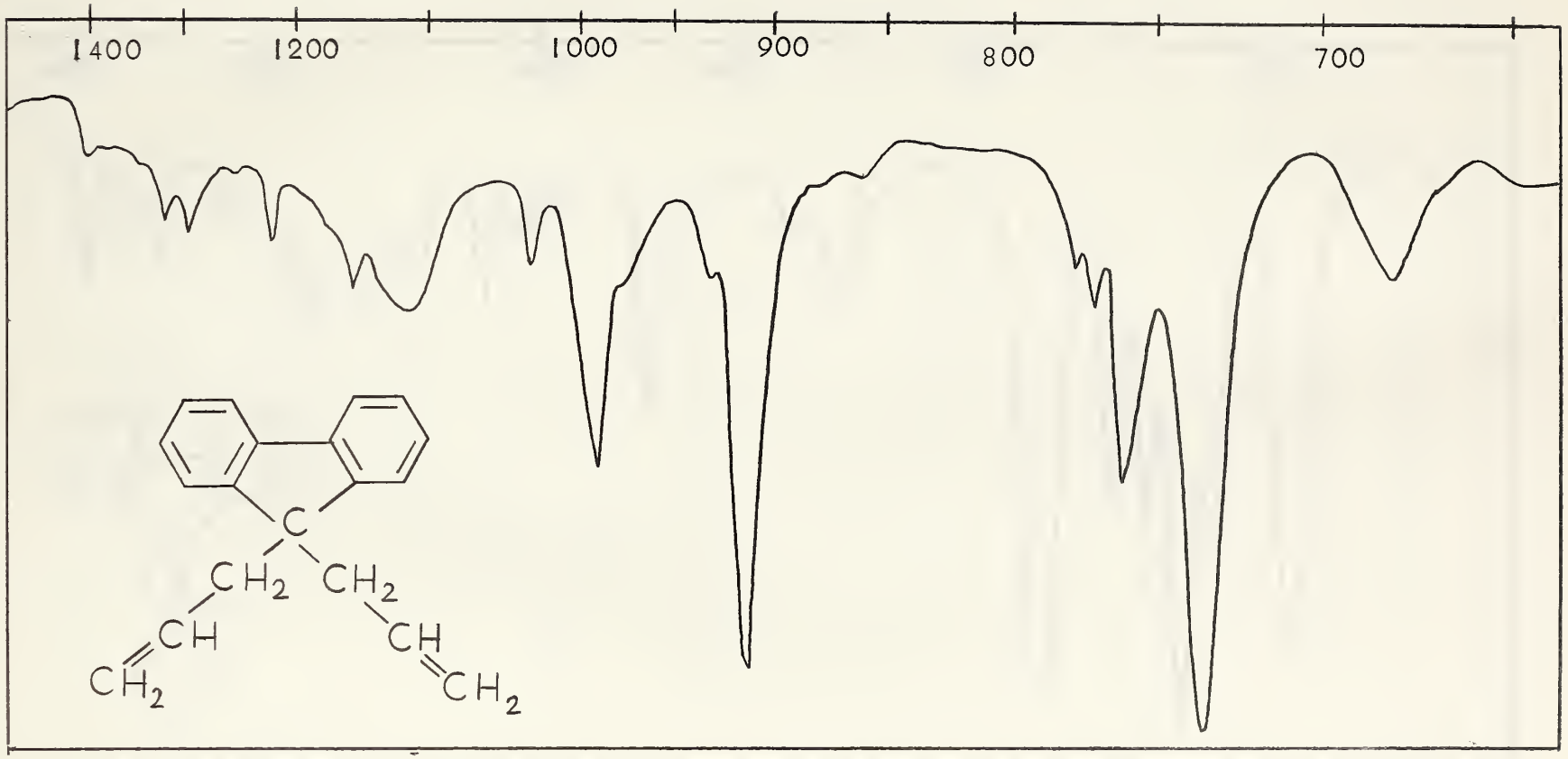


Fig. 14 Partial infrared spectrum of 9,9-diallylfluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

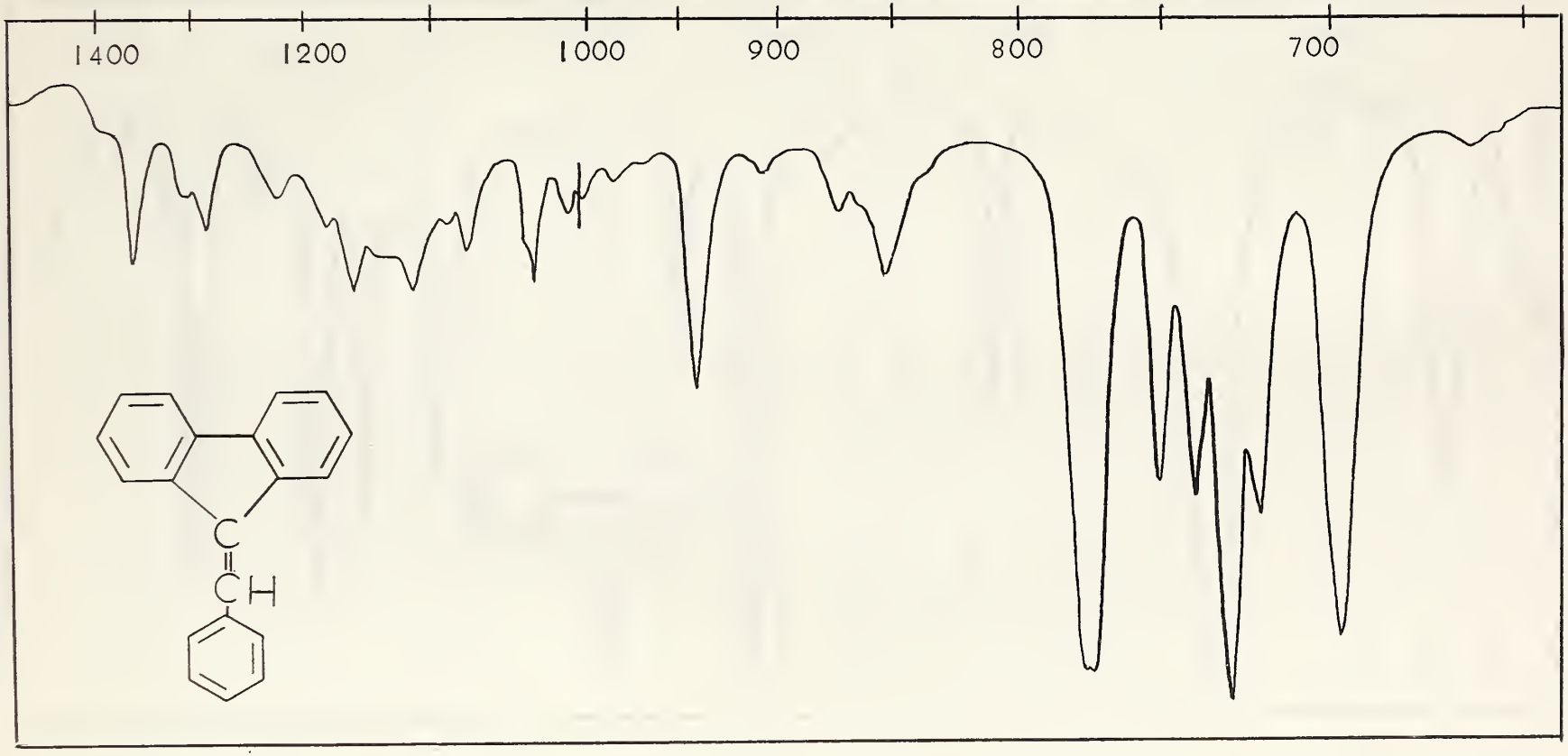


Fig. 15 Partial infrared spectrum of 9-benzylidenefluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

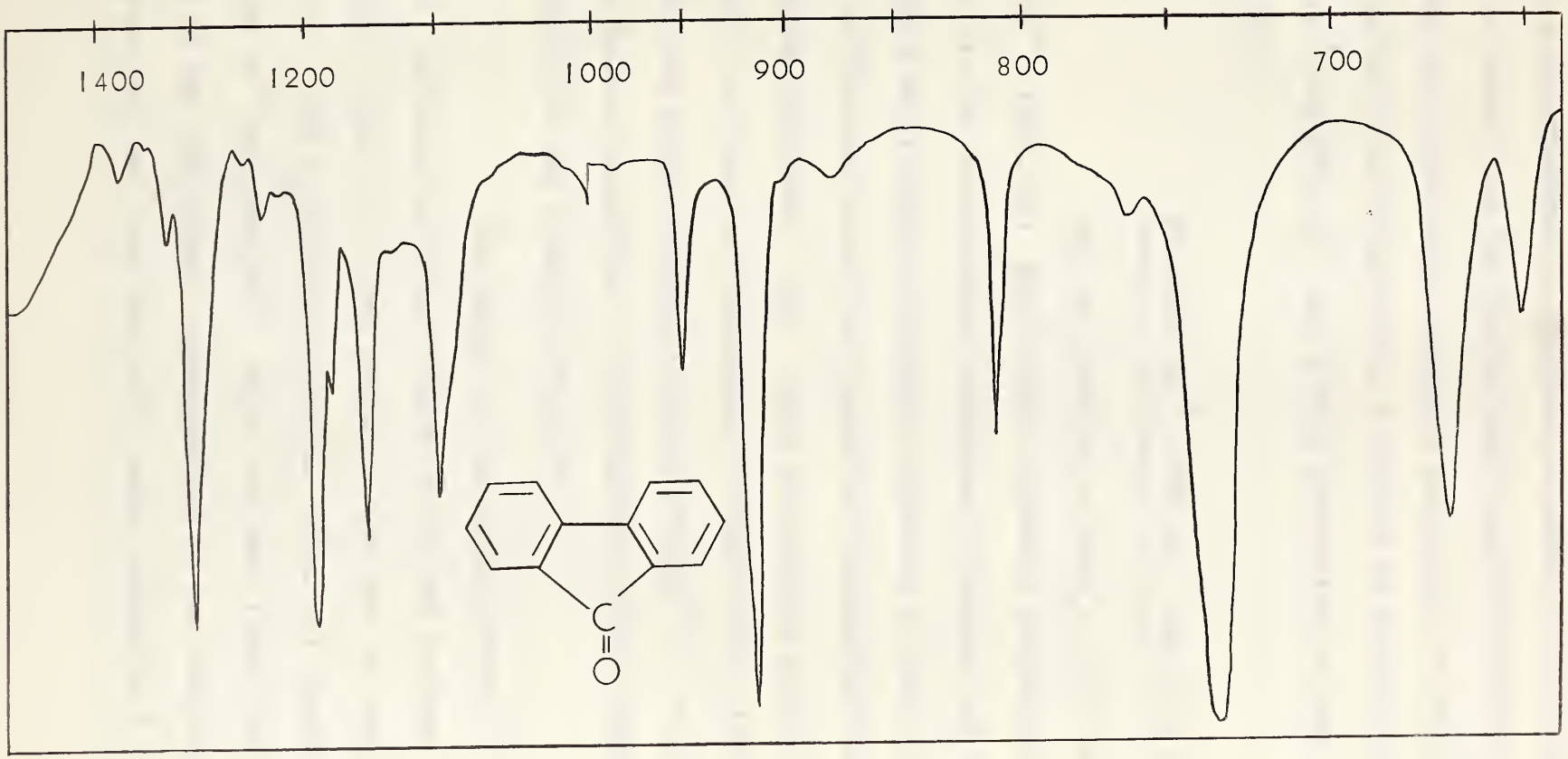


Fig. 16 Partial infrared spectrum of 9-fluorenone in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

The absorption band at 2930 cm^{-1} is not shown on the spectrum of fluorene in carbon tetrachloride solution taken with the Perkin Elmer spectrophotometer model 221. Instead, with this high resolution instrument two bands appear at slightly lower frequencies, a doublet of medium intensity at 2901 cm^{-1} and 2885 cm^{-1} and a weak absorption at 2795 cm^{-1} (Fig. 21).

The 2901 cm^{-1}, 2885 cm^{-1} and 2795 cm^{-1} Bands.

The two absorption bands at 2901 cm^{-1} and 2885 cm^{-1} (Fig. 21) most likely represent respectively the asymmetric CH_2 out-of-phase stretching vibration and the symmetric CH_2 in-phase stretching vibration of the methylene group of fluorene since they appear at frequencies characteristic for these vibrations (39). Since deuteration reduces these bands markedly, but does not completely eliminate them, (there remains a weak, but broad absorption around 2900 cm^{-1}), it appears that the methylene absorption is superimposed on some other weaker absorption of the fluorene structure.

The bands for the corresponding C-D bonds appear within the expected region (Table 1). In the spectrum of C_9-deuterofluorene (Fig. 22) there appears a new band of weak intensity at 2175 cm^{-1}. The C_9-dideuterofluorene (Fig. 23) shows two new bands at 2190 cm^{-1} and 2120 cm^{-1}, which are most likely the absorption bands of the $>CD_2$ group, corresponding to the two bands of the $>CH_2$ group at 2901 cm^{-1} and 2885 cm^{-1}, which indicates a shift by a factor

in agreement with the factor established in the literature (38). Fluorene shows another absorption band in the C-H stretching region at 2795 cm^{-1}, which is certainly associated with the methylene group since it is clearly eliminated upon deuteration (Figs. 21 - 23). Weak absorption between 2700 cm^{-1} and 2800 cm^{-1} has been quoted to stem from interaction of the aromatic C-H stretching vibration and the methylene deformation modes of vibration (38, 39).

Useful Bands Associated with Particular Substituents at C_9 of Fluorenes.

In all the spectra (Figs. 1 - 16) there is clearly discernible a characteristic strong band at 738 cm^{-1} originating from the two ortho disubstituted benzene nuclei in fluorene (38).

Monomethyl-, monobenzyl- and monoallylfluorene as well as 9-benzylidenefluorene all show weak absorption in the region of 787 cm^{-1} to 793 cm^{-1} and medium strong absorption in the region of 719 cm^{-1} to 728 cm^{-1} (overlapping to some extent with the major 738 cm^{-1} band). Only for the monomethylfluorene is this latter absorption of weaker intensity, though still quite readily discernible, and the former stronger than in all other cases examined. Disubstitution at C_9 removes this absorption completely. These two bands are attributed to the remaining C_9-H bond, since they are also eliminated upon deuteration. The 719 cm^{-1} to 728 cm^{-1} band has been used to differentiate between the mono- and disubstitution and, in particular, to follow

the preparation, purification and identification of 9-monoallylfluorene and 9,9-diallylfluorene whose mixtures with each other and with fluorene itself are separated with difficulty. Clear distinction of the methylated fluorene from the allyl- or benzyl fluorenes may be made by observation of the strong, isolated band at 758 cm^{-1} in the spectrum of monomethylfluorene, which doubles in intensity upon dimethylation. The monomethyl compound shows another medium-weak, though impressive, band at 793 cm^{-1}, which is eliminated upon dimethylation or deuteration of the remaining C_9 - H. Allylfluorenes absorb at 913 cm^{-1}, the intensity of the diallyl compound being approximately double that found for the monosubstituted derivative. This absorption is no doubt that associated with the C-H out-of-plane bending found in olefinic structures (38). The band appearing at 681 cm^{-1} for mono- and diallylfluorene may also be of analytical value.

The strong absorption at 700 cm^{-1} in 9-benzylfluorene (approximately doubled in the corresponding dibenzylfluorene) is due to the monosubstituted benzene moiety. Also of some assistance in identifying 9-benzylated fluorene is the weak band at 905 cm^{-1} to 909 cm^{-1}. This appears to be present in 9-benzylidenefluorene too. Whether the same absorption is to be found in the allylfluorenes cannot be shown since the strong 913 cm^{-1} band interferes. Of some assistance is the strong absorption at 761 cm^{-1} to 764 cm^{-1} for diallyl- and dibenzylfluorene, whereas for the monoallyl- and monobenzylfluorene a similar strong

band occurs at 754 cm^{-1}. Furthermore, a band at 746 cm^{-1} to 748 cm^{-1} appears for the mono- and dibenzylfluorene but not for mono- and diallylfluorene.

Considerable effort has been made to purify monobenzylfluorene in order to eliminate the small amount of fluorene indicated by the presence of weak absorption at 952 cm^{-1}, but neither repeated recrystallization from alcohol nor repeated fractionation of the material on a chromatographic column removed this band. Since each fraction emerging from the column retained the same intensity at this frequency, it is possible that it does not represent contaminating fluorene, but could be part of the absorption of monobenzylfluorene, probably a combination band of the remaining C_9-H and of the $-CH_2-$ of the benzyl substituent, for it does not appear in deuterated monobenzylfluorene nor in dibenzylfluorene (Figs. 11, 12). It is rather surprising that the monoethylfluorene (Fig.8) shows no absorption at 719 cm^{-1} to 728 cm^{-1}, which was quite characteristic for C_9-monomethyl, -benzyl and -allylfluorene. The C_9-monobutylfluorene also failed to show absorption in this region. This spectrum is not reported here because only the 9,9-di-n-butylfluorene could be obtained spectroscopically pure. The monobutyl derivative resisted complete purification although several attempts at chromatographic separation were made.

Of extreme importance for this work were the spectra of methylfluorenes, because methylation has been used

extensively to evaluate the extent of metalation. Low concentrations of monomethylfluorene in, say, 9,9-dimethylfluorene are not detectable by the absorption at 719 cm^{-1} due to the masking effect of the very strong band at 738 cm^{-1}, stemming from the orthodisubstituted benzene rings of fluorene. For this situation the weak band at 793 cm^{-1} is more satisfactory since it is quite clearly distinguishable even at low concentrations. The most significant bands used for product determination later in this work are compiled in Table II.

The small region from 1050 to 1110 cm^{-1} (9.0 - 9.5μ) is also quite helpful for the determination of methylated fluorenes, especially to detect small amounts of dimethylfluorene mixed with monomethylfluorene and unsubstituted fluorene. This absorption is not strong but quite sharp and distinct. Dimethylfluorene shows a band at 1078 cm^{-1} (with a smaller one at 1085 cm^{-1}). Monomethylfluorene shows no absorption at these positions but in turn exhibits sharp, though weak absorption at 1098 cm^{-1}, while fluorene absorbs only at 1089 cm^{-1} in this region (Fig. 19).

For the evaluation of the deuteration experiments the importance of the three bands in the 600 cm^{-1} to 700 cm^{-1} region should be emphasized. These three bands, at 694, 677 and 667 cm^{-1}, which represent the $>CH_2$, $>CHD$ and $>CD_2$ groups respectively, occur with approximately equal intensity on the spectra of the pure compounds and hence their integrated

absorption areas allow a quantitative determination in cases where the product consists of a mixture of the three materials. This is of great assistance since it would be quite difficult to evaluate these quantities.

Summary.

An investigation of the C-H deformation region of the infrared spectra of fluorene and C_9-substituted derivatives revealed that the bands at 1400, 1298, 952 and 692 cm^{-1} are associated with the methylene group of fluorene. These bands were either eliminated or reduced markedly in intensity upon deuteration or alkylation at C_9.

Since some bands in the spectra of C_9-monosubstituted fluorene derivatives were eliminated by deuteration or further substitution at C_9, they are most likely due to the remaining hydrogen at this position. Thus the C_9-H was found to absorb at 719 and 793 cm^{-1} in 9-methylfluorene, at 720 cm^{-1} in 9-benzylfluorene and at 727 cm^{-1} in 9-allylfluorene.

Several new bands appearing in the spectra of C_9-mono- and dideuterated fluorene could be related to the $>$CHD and $>CD_2$ units. The bands at 974, 827 and 667 cm^{-1} were found to be characteristic for the $>CD_2$ group, while that at 677 cm^{-1} could be related to the $>$CHD group. Both groups appear to absorb at 939 cm^{-1}.

The C-H stretching region, under high resolution, showed two bands, 2901 and 2885 cm^{-1}, which were associated with

the methylene group of fluorene. The corresponding C-D band of monodeuterated fluorene was found to absorb at 2175 cm^{-1}, while two such bands at 2190 and 2120 cm^{-1}, were found in the spectrum of dideuterated fluorene.

In addition, fluorene showed a weak, but characteristic combination band at 2795 cm^{-1}.

Table II

Characteristic Absorption Bands in the Infrared Spectra of C_9-Substituted Fluorenes (cm^{-1})

Methyl-		Ethyl-[b]	
mono-	di-	mono-	di-
-	-	658 m	nil
719 m	nil	nil	nil
-	-	735-740 (broad)	735-740 (narrow)
758 s[a]	758 s[a]	-	-
793 s	nil	nil	nil
nil	nil	820 w	nil
nil	nil	838 w	nil
-	-	869 mw[a]	869 mw[a]
-	-	-	925 m[a]
932 m	932 m	-	-

continued ...

Table II, continued

Benzyl- mono-	Benzyl- di-	Allyl- mono-	Allyl- di-
-	-	681 mw[a]	681 mw[a]
700 s[a]	700 s[a]	-	-
720 ms	nil	-	-
-	-	727 ms	nil
746-748	746-748	-	-
754 s	nil	754 s	-
nil	761 - 764 s	-	761-764 s
905-909 m[a]	905-909[a]	-	-
-	-	913 s[a]	913 s[a]

m = medium, s = strong, w = weak

(a) The disubstituted compounds absorb approximately twice as much as do the monosubstituted fluorenes and have broader bands.

(b) In addition, the monoethyl compound shows two strong bands at 748 and 760^{-1}, the former more intense than latter. The diethyl compound shows strong absorption at 754 and 760 cm^{-1}, the latter stronger than the former.

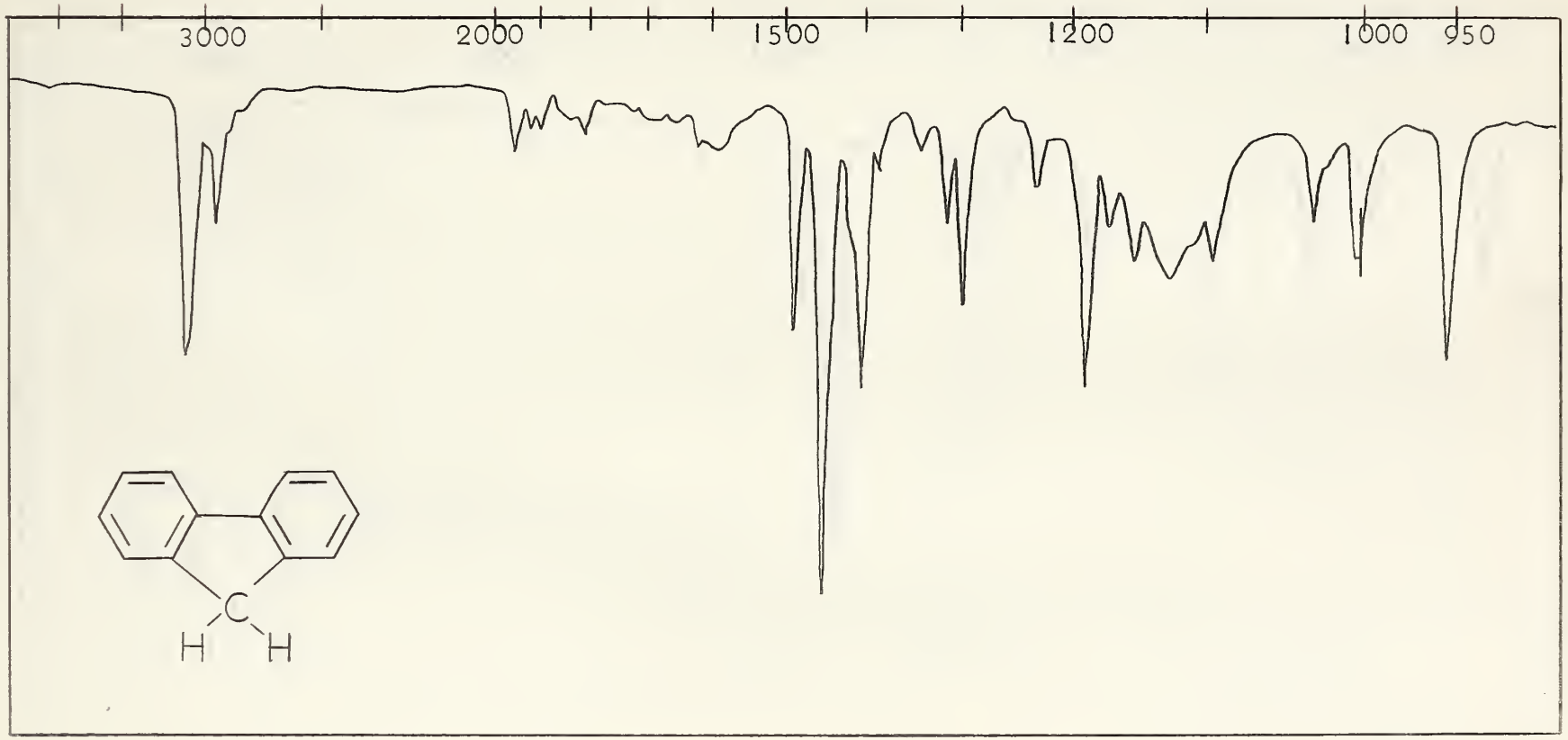
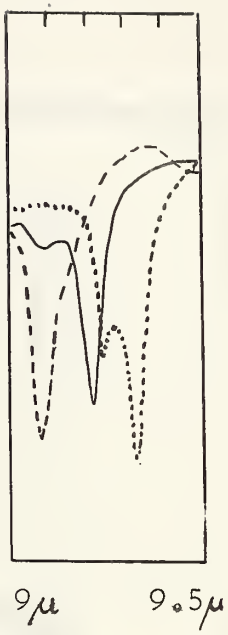


Fig. 17 Partial infrared spectrum of fluorene in CCl_4 showing the 4000-900 cm^{-1} region (Perkin Elmer21)

Fig. 18 Partial Infrared spectrum of 9-deuterofluorene in CCl_4 showing the 4000-900 cm^{-1} region (Perkin Elmer 21)

Fig. 19

Partial infrared spectrum of fluorene, 9-methylfluorene and 9,9-dimethylfluorene in CS_2 showing the 9-9.5μ region (Perkin Elmer 21)



——— fluorene
- - - - - - - 9-methylfluorene
. . . . . 9,9-dimethylfluorene

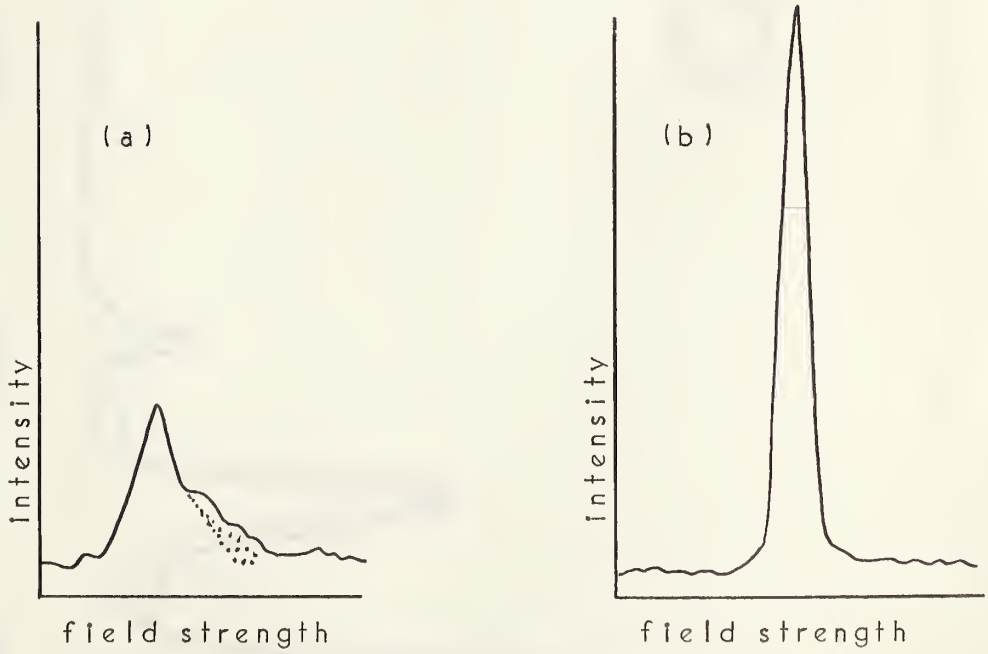


Fig. 20 Partial NMR spectra of (a) 9-deuterofluorene and (b) fluorene showing the CHD and CH_2 bands

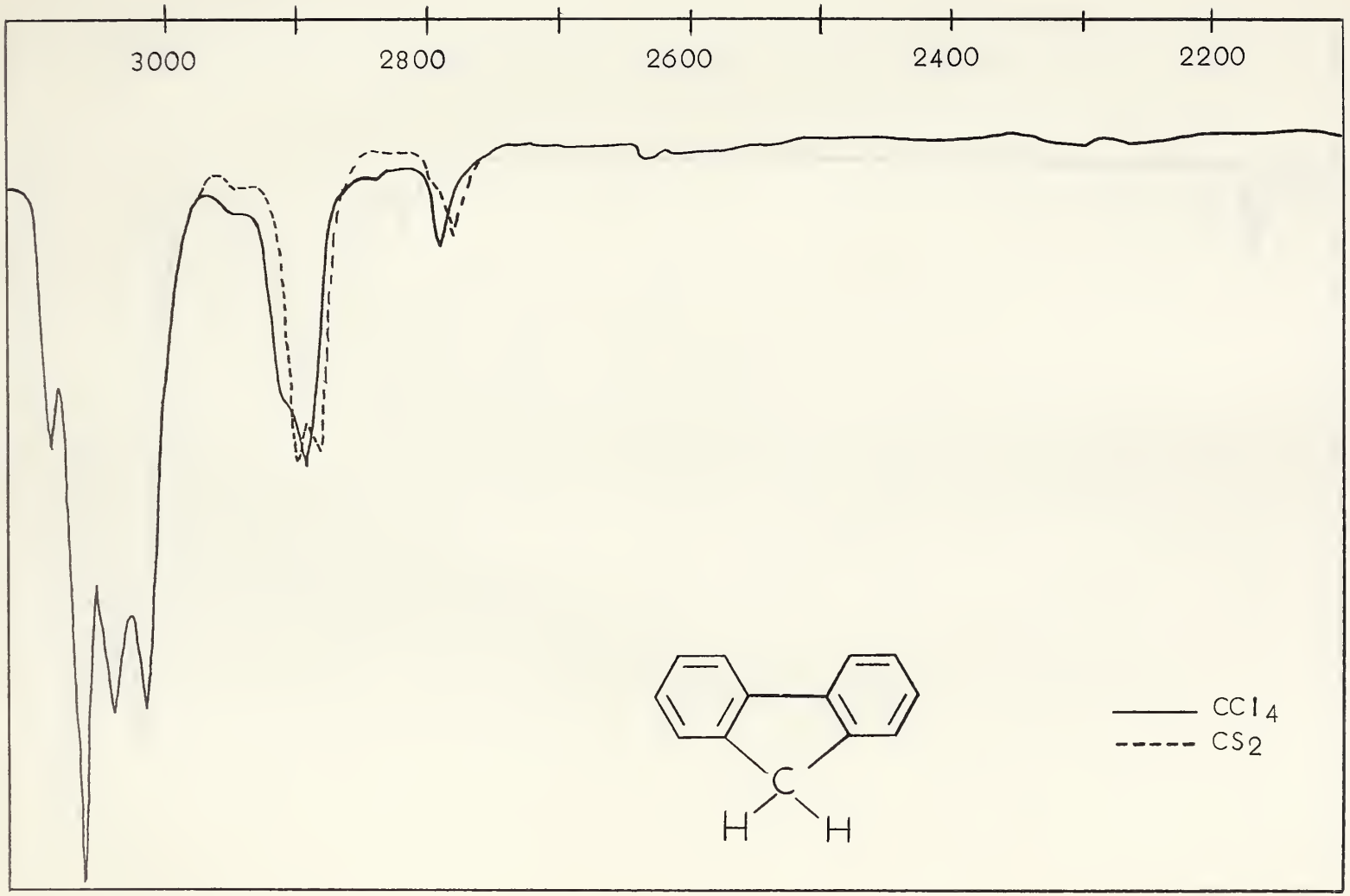


Fig. 21 Partial infrared spectrum of fluorene in CCl_4 and CS_2 showing the 3100-2100 cm^{-1} region (Perkin Elmer 221)

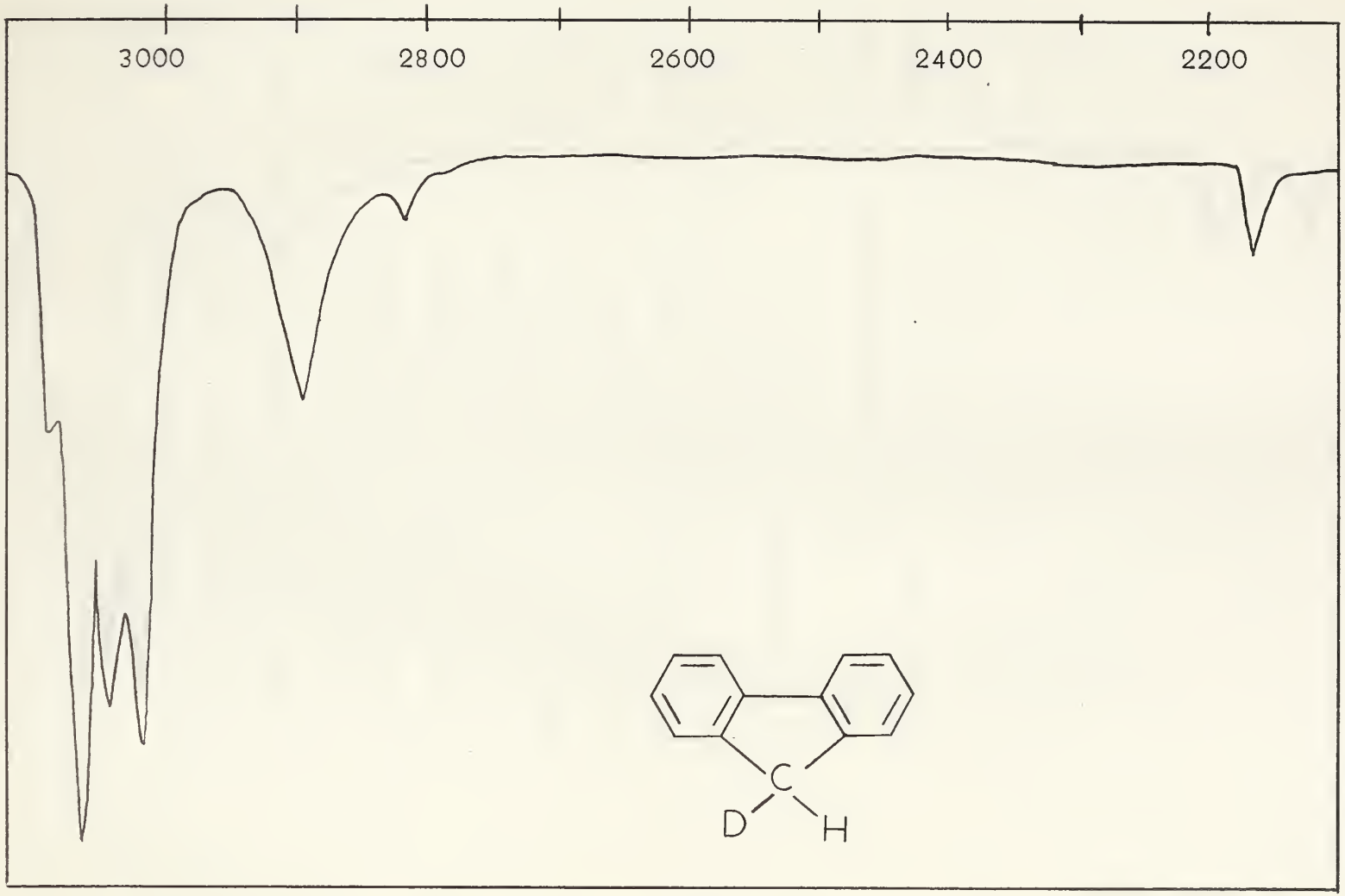


Fig. 22 Partial infrared spectrum of 9-deuterofluorene in CCl_4 showing the 3100-2100 cm^{-1} region (Perkin Elmer 221)

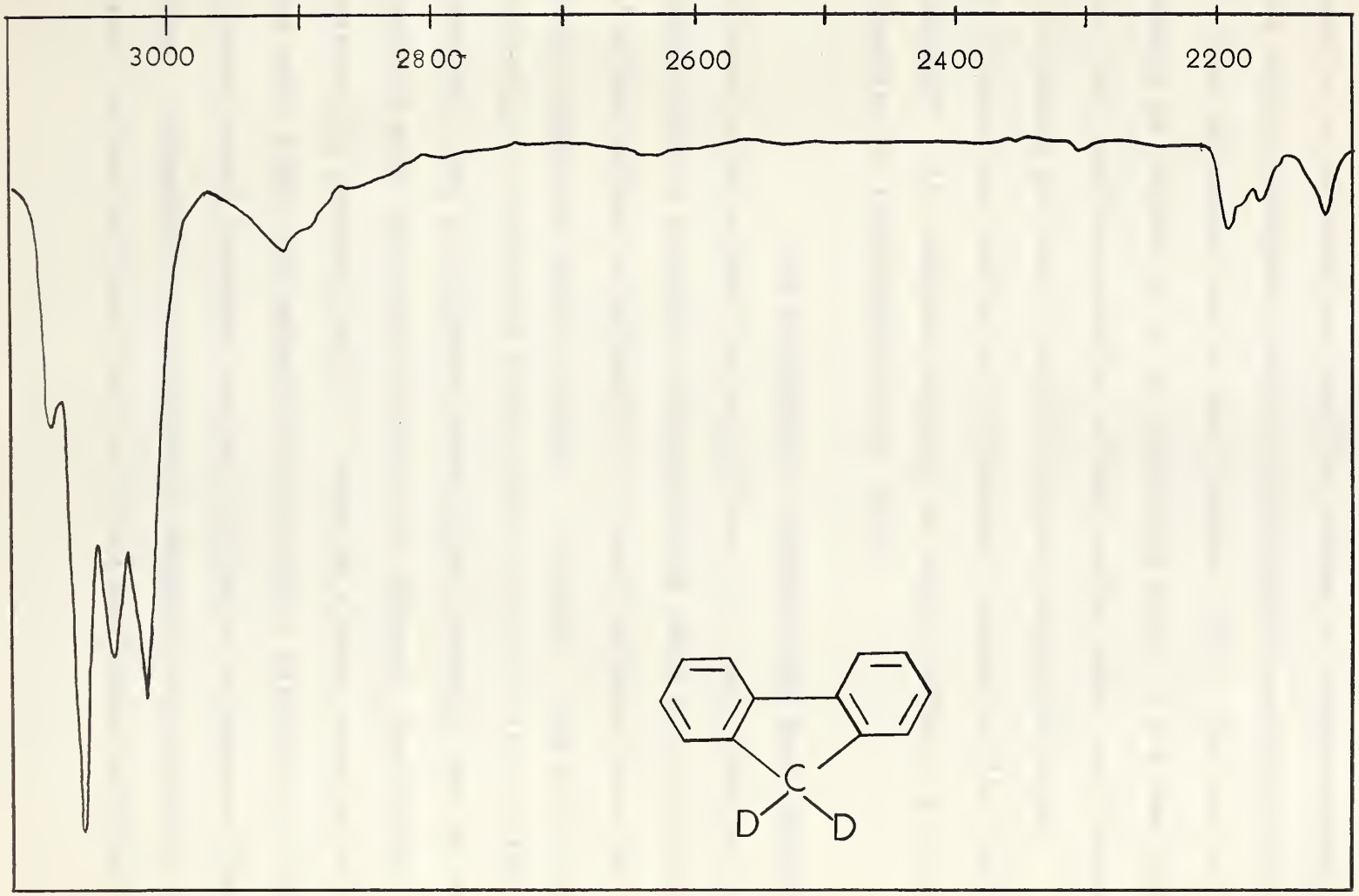


Fig. 23 Partial infrared spectrum of 9,9-dideuterofluorene in CCl_4 showing the 3100-2100 cm^{-1} region (Perkin Elmer 221)

2. The Metalation of Fluorene by Alkali Metals.

The formation of 9-fluorenylsodium by direct reaction of fluorene and metallic sodium, although reported in the patent literature, has been found highly unsatisfactory both in this laboratory and by other workers (19). The use of liquid ammonia as solvent is of no assistance since it had been shown that the reaction occurring between sodium metal and fluorene in this medium was one of addition rather than substitution. No hydrogen was evolved and subsequent reaction of the "addition compound" with ammonium chloride or methyl iodide led to the formation of dihydroderivatives (22).

No satisfactory procedure has been reported hitherto which allows the preparation of a pure potassium- or sodium salt of fluorene. Crossmetalation using alkyl derivatives of alkali metals is unfavorable for many purposes since the metal reagent is usually prepared "in situ" from alkyl halides. Obviously any unreacted alkyl halide will give rise to side products, such as undesired substituted fluorenes, due to the reaction with the metal derivative of fluorene. Furthermore undesirable products could be formed by a Wurtz reaction between the metal alkyl and unreacted alkyl halide. Mixtures of different C_9-substituted fluorenes are very difficult to separate from each other. Furthermore the presence of inorganic side products such as metal halides has been found to effect metalation reactions (40).

Accordingly the possibility of direct reaction of alkali metals with fluorene in various solvents was investigated.

a) Metalation of Fluorene with Potassium in Common Ether Solvents.

Since the preparation of Grignard compounds (41) occurred quite readily in diethyl ether but with much greater difficulty in nonpolar solvents such as hydrocarbons, one might expect similar results for the metalation of fluorene by alkali metals.

Several attempts were made to bring about reaction of potassium metal with fluorene in diethyl ether solution. However the yields of substituted fluorenes from the reaction of the 9-fluorenylpotassium and methyl iodide or benzyl chloride indicated that the organometallic compound had formed only to a small extent. Diisopropyl ether, di-n-butyl ether and anisole, having boiling points higher than the melting point of potassium, in the four to five hours usually allotted for the reaction between the metal and fluorene in each experiment in order to compare the relative efficiencies of the solvents, caused apparently complete or nearly complete disappearance of the metal and precipitation of the brown or reddish-brown 9-fluorenylpotassium. However, this was deceiving, since in some cases the metalated compound, incompletely formed, occluded unreacted potassium which was liberated as the grey metal in subsequent reaction of the organometallic compound with alkyl halides. The reddish-brown 9-fluorenylpotassium reacted more

rapidly than did the liberated potassium with the alkyl halide thus permitting the particles of potassium metal to be clearly discernible for a short time.

With di-n-butylether as solvent it was shown that longer reaction times increased the yield of organometallic compound. During 12 hours in refluxing di-n-butyl ether potassium metalated fluorene to an extent of 50 per cent as determined by the methylation technique. On the other hand only 25 per cent reaction had occurred during a period of 5 hours under otherwise identical conditions. Because of the low boiling point of diethyl ether, completion of the reaction in this solvent required a much longer time.

Significant reaction of the solid potassium metal with fluorene occurred in some ethers even at room temperature. Diethyl ether, during a period of 24 hours, caused "complete" disappearance of the potassium and the formation of the brown 9-fluorenylpotassium to the extent of 60 per cent, as indicated by the extent of methylation. In butyl ether or anisole, however, insignificant amounts of the methylated fluorene were found. This is not surprising in case of anisole, since this ether can itself be readily metalated (40, 42), hence it might react with the 9-fluorenylpotassium just formed, thus regenerating fluorene. This possibility was not investigated since other lines of experimentation proved more profitable. Diphenyl ether at 100° C apparently brought about reaction of potassium and fluorene, as

judged by the precipitation of a brown compound and the simultaneous disappearance of the metal, however a tarry material was finally obtained. The sluggishness of the subsequent reaction of this tarry material with an alkyl halide, as well as the difficulty experienced in separating the mixture of fluorene, 9-substituted fluorene and the high boiling diphenyl ether led to the elimination of diphenyl ether as a suitable solvent for this reaction. The results obtained with the various ether solvents are summarized in Table III.

Table III

Reaction of Potassium and Fluorene in Various Ethers.

Solvent	Conditions	Amount K apparently consumed	Amount of methylation[c] (%)
diethyl ether	22°, 24 hrs.	complete	60
di-n-butyl ether	22°, 24 hrs.	very little	--[b]
di-n-butyl ether	reflux, 5 hrs.	incomplete	25
di-n-butyl ether	reflux, 12 hrs.	incomplete	50
diisopropyl ether	reflux, 5 hrs.	incomplete	20
anisole	22°, 24 hrs.	very little	--[b]
anisole	100°, 4 hrs.	complete[a]	15
diphenyl ether	100°, 4 hrs.	complete[a]	--[b]

(a) A tarry brown material formed, which included unreacted potassium.

(b) The amount of 9-fluorenylpotassium formed was too small to justify methylation.

(c) Estimated by reaction of 9-fluorenylpotassium with methyl iodide and subsequent chromatographic separation of an aliquot of the reaction product.

b) The Metalation of Fluorene by Potassium in Dioxane.

It was found at a very early stage of this work that potassium metal reacts readily with fluorene in boiling dioxane as the solvent. Protection of the 9-fluorenylpotassium by an atmosphere of nitrogen was necessary. Hydrogen gas was evolved during the reaction and a reddish-brown solution was formed, precipitating a reddish-brown substance as the reaction proceeded. Starting with 0.05 moles of the reagents in 50 ml of dioxane the reaction was apparently complete after four hours, i.e. no unreacted metal seemed to be left. Cooling to room temperature precipitated most of the 9-fluorenylpotassium. This precipitate could be freed of unreacted fluorene by filtration and washing with dry hexane. The monopotassium derivative, obtained by the reaction of equimolar proportions of potassium and fluorene, could be isolated under nitrogen as a solid quite suitable for further reaction. The presence of particles of unreacted potassium was found to accelerate the decomposition of the organometallic compound. Hence it was advisable to carry the reaction to completion with respect to the metal. Usually it was more convenient to leave the solid suspended either in the original dioxane, or in hexane wash liquid, where it could be kept for some time with little decomposition. Exposure to air caused rapid decomposition of this metalated product to a dark mass which was found to consist of potassium hydroxide, fluorenone, 9-fluorenol and fluorene, the

relative amounts of these depending upon the accessibility to oxygen or water from the air.

Attempts to analyze the isolated 9-fluorenylpotassium gave low values for potassium, presumably due to absorption of water and/or oxygen from the air during weighing manipulations. Three analyses gave an average value of 15.3 per cent of potassium, whereas the calculated value is 19.5 per cent.

The reaction of the 9-fluorenylpotassium, prepared in dioxane at reflux temperature during a period of four hours, with methyl iodide indicated that the extent of metalation was at least 80 per cent.

The metalation of fluorene by potassium metal in dioxane occurred even at room temperature, although much more slowly. The addition of methyl iodide to the organometallic compound, prepared during a period of stirring of 12 hours at 22°, indicated that only 30 per cent metalation had occurred despite the apparent complete consumption of all potassium metal.

c) Estimation of the Extent of Metalation of Fluorene by Potassium.

Yields obtained in the various metalation experiments were determined on the basis of the amount of 9-substituted fluorene, usually the methylated compound, actually

isolated after treatment of the organometallic product with a suitable organic halide. The separation of methylated fluorene from unreacted fluorene was performed by elution chromatography on a column packed with alumina. Pentane or hexane was used as eluent. Since disubstituted fluorene was produced along with monosubstituted fluorene, as will be reported in detail later in this work, this was taken into consideration in determining the extent of metalation.

The methylation technique would tend to give slightly lower values for the metalation due to small losses from incomplete reaction of the metal derivative of fluorene with the halide. Losses from isolation procedures were avoided by the use of the aforementioned chromatographic separation of a sample of the product. This technique was extensively used throughout this work.

Another convenient method for estimating the extent of metalation was at first thought to be one in which the metal derivative of fluorene was allowed to react with deuterium oxide and the deuterated products then examined by infrared spectroscopy. The bands at 952 cm^{-1} and 692 cm^{-1} for fluorene and those at 667 cm^{-1} and 677 cm^{-1} for the mono- and disubstituted fluorene respectively are especially useful for this purpose.

However, there existed the possibility that the deuteration technique might give somewhat higher values for the amount of organometallic compound formed due to the occurrence of

isotope exchange between fluorene and deuterium oxide in the presence of the base MOD formed during the reaction of metal fluorenyl and D_2O. This possibility was considered and a careful examination, which will be reported later, showed that such an exchange did occur in some cases to a much larger extent than anticipated. Hence it was clear that the estimation of the degree of metalation of fluorene with alkali metals via deuteration would lead to erroneous results and consequently could not be employed.

d) Metalation of Fluorene by Potassium in Hydrocarbon Solvents.

No significant reaction was observed between fluorene and potassium in refluxing hydrocarbons such as heptane, xylene, toluene or benzene. Even refluxing decalin, the solvent used to prepare 9-fluorenylsodium from fluorene and sodamide (19), failed to promote the formation of the organometallic compound. Instead, the potassium metal remained finely divided and apparently unreacted. Only a very small amount of the brown potassium fluorenyl was formed, much too little to justify any subsequent reaction with methyl halide.

However when dioxane was added to these inert solvents to the extent of twenty per cent, the usual reaction of the potassium metal was observed in the refluxing mixture, though more slowly and incompletely in the four to five hour reaction time. Following the addition of an appropriate alkyl halide, the yields of 9-substituted fluorenes were about

one third to one half of those obtained in pure dioxane. At room temperature , these dioxane-hydrocarbon mixtures gave insignificant reaction. When ethers other than dioxane were added to the hydrocarbon solvent (e.g. di-n-butyl ether, diethyl ether, anisole) the yields of 9-substituted fluorene after alkylation dropped to less than five per cent. These results agree with the known fact that mixtures of ethers and hydrocarbons are inferior to the pure liquid ethers as solvents for Grignard preparations (41).

When dioxane was added to xylene or toluene to the extent of one per cent, practically no reaction occurred at the usual reflux temperature even for extended reaction time.

e) Attempted Metalation of Fluorene with Sodium or Lithium in Dioxane.

When metallic sodium (m.p. 97.5°) replaced potassium in refluxing dioxane (b.p. 101°/760 mm) or di-n-butyl ether (b.p. 142°/760 mm) containing dissolved fluorene, some reaction did occur in the four to five hours time allotted , since the metal slowly became coated to a small extent with a reddish brown material. The dioxane solution became only faintly yellow. Further reaction apparently ceased and even extended reflux time (12 hours) and more vigorous stirring to subdivide the metal, which is molten in di-n-butyl ether but just solid in dioxane, failed to cause any significant additional reaction. The product, alkylated as usual, gave a very low yield

(0 - 5 %) of 9-substituted fluorene.

In the case of metallic lithium (m.p. 186°), cut into small pieces as was sodium, little reaction was observed in the usual four to five hours. The surface of some pieces of the metal did accumulate a yellow-orange coating but most of the particles remained apparently unaffected. The dioxane solution did take on a faint yellow coloration. When the reaction was allowed to continue for sixteen hours, the solution became somewhat reddish-brown. However, following the usual treatment with methyl iodide most of the metal was found to have been unreacted and only about five per cent yield of methylated fluorene was obtained.

Since it is known that these metals do react more readily when they are in a finely divided state, an experiment was devised to illustrate the effect of the state of subdivision of the metal on its reaction with fluorene in dioxane. Sodium (0.05 mole) was dispersed by rapid stirring in boiling xylene and lithium (0.05 mole) in boiling decahydronaphthalene. The state of subdivision was maintained while the liquids were cooled. The dispersing liquids were replaced by dioxane, an equimolar amount of fluorene added and the solutions refluxed and continually stirred. At the boiling point of dioxane (at our pressure of 700 mm) the sodium was just solid but the particles of metal showed a strong tendency to stick together in spite of the vigorous stirring, a phenomenon observed also with the larger

pieces of sodium used previously. On the other hand, the particles of lithium, less than half a millimeter in diameter, remained subdivided in boiling dioxane. By visual observation the average size of the sodium particles was estimated to be about ten times that of the lithium particles. In four hours time the metallic sodium showed only slight surface coloration. This was similar to the previous observations noted above and not unexpected since roughly the same extent of subdivision of the metal occurred in both cases in refluxing dioxane, due to the tendency of the particles to stick together. Thirty hours of continual reflux and stirring followed by alkylation as usual indicated less than five per cent metalation. The much more finely divided lithium in boiling dioxane showed evidence of reaction in four hours by a slight reddish coloration of the dioxane. Thirty hours reflux followed by alkylation, showed that approximately eight per cent metalation had occurred.

It is clear that the extent of subdivision of the metal does affect its reactivity with fluorene. It was also clearly demonstrated that, when larger pieces of potassium, sodium or lithium metal of similar size were allowed to react with fluorene in dioxane at room temperature, only the potassium showed significant reaction. In an experiment wherein potassium had disappeared in 24 hours at room temperature, no visible reaction occurred for the sodium or lithium under identical conditions and in the same time. The same larger pieces of sodium

and lithium in boiling dioxane showed clearly a slight reaction for sodium and less (or none) for lithium, as judged by the appearance of the metal surface and the color of the solution. From these observations it is quite apparent, that under comparable conditions in dioxane solvent potassium is much more reactive than sodium and lithium and that sodium and lithium are not much different from each other in reactivity.

f) The Metalation of Fluorene by Alkali Metals in 1,2-Dimethoxyethane, 1,2-Diethoxyethane and Tetrahydrofuran.

Since of the common ether solvents examined dioxane was the most effective and especially because addition of ethers to the normally ineffective hydrocarbons to the extent of twenty per cent gave reaction of the potassium metal in fluorene in case of dioxane, but not in case of dialkyl or aryl-alkyl ethers, it was thought that the presence of two ether oxygen atoms in a single molecule, suitably situated as in the unstable boat form of dioxane and / or sterically less hindered oxygen atoms (43) are responsible for the preferred reaction found for dioxane. This viewpoint, augmented by the reports that certain ethers such as those of ethylene glycol (44, 45) dissolve small amounts of potassium metal at low temperatures to form blue, electrically conducting solutions, while dialkyl

ethers do not, led to the investigation of the comparative efficiencies of ethers of ethylene glycol, as well as tetrahydrofuran as solvents for the reaction of the alkali metals, lithium, sodium and potassium with fluorene. The following section describes results of experiments in this direction.

As already mentioned in the literature review, Gilman and Gorsich (23) have used tetrahydrofuran as a solvent to facilitate the preparation of the addition compound of sodium to naphthalene, a compound which then metalated various hydrocarbons. However, the presence of naphthalene and the dihydronaphthalene byproduct of these metal addition reactions complicated isolation and purification of the desired reaction products after subsequent reaction of the organometallic compound with suitable reagents. The results of the present work show that in the case of fluorene, the hydrocarbon under investigation, the addition of naphthalene is an unnecessary factor in the reaction of the alkali metals with fluorene to form the organometallic compound by replacement of hydrogen.

For the comparative studies equivalent amounts of metal and fluorene were used in the appropriate solvent. The particular quantities upon which time and extent of reaction are quoted, were 0.05 moles of fluorene, 0.05 gramatoms of the metal and 50 ml of the solvent. The reactions were protected by

nitrogen atmosphere and anhydrous conditions were employed all the time. The results are compiled in Table IV for convenience. The metals lithium, sodium and potassium were studied, while the solvents were 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE) and tetrahydrofuran (THF). For those cases where the metal remained solid under the conditions employed, care was taken to use pieces of roughly similar size, about 1 mm^3. Solid pieces of sodium, especially at higher temperatures, had a strong tendency to stick together, hence presenting a smaller surface area to the reagent than was originally obtained. Molten sodium did not show this property. A similar behavior for potassium was not found, probably due to the greater rate of reaction of fluorene at the surface preventing adhesion of metal particles. Lithium particles did not stick together at all.

In DME potassium (m.p. 62°) reacted with fluorene quite readily even at room temperature (22°). The dark red 9-fluorenylpotassium began to accumulate on the surface of the metal as soon as the compounds were put together and could be removed by agitation of the solvent in which the salt dissolved quite easily. The exothermic reaction of the metal with fluorene at 22° was sufficiently rapid to raise the temperature of the solution to the point where the metal liquified. Hence a cooling bath was required to control the temperature. When stirred for about two hours at room temperature, the metal dissolved completely. The rate of solution is dependent in part upon the degree of

agitation of the solutions and the surface area of the metal. However, even larger pieces of the metal reacted quite readily. In boiling DME ($85^{\circ}/700$ mm) at which temperature the potassium is molten, complete solution occurred within one hour or less.

With sodium (m.p. 97°), fluorene gave evidence of reaction in DME solvent also at room temperature. In one hour at 22° the solution showed definite red coloration due to the dissolved 9-fluorenylsodium and in 8 hours the solution of the metal appeared to have been complete. In refluxing DME solution sodium reacted completely in 10 hours. The longer time required at higher temperature may be due to the increased tendency for adhesion of the softer metal particles.

Lithium metal (m.p. 186°) reacted at least as readily with fluorene in DME as did metallic sodium. At room temperature appearance of red color on the surface of the metal was noticed within 30 minutes and complete reaction occurred in 5 hours. At reflux temperature of DME, the surface of the lithium colored within 15 minutes but still approximately 5 hours were required to dissolve the metal completely, even though the particles of lithium did not stick together. The impression is gained that lithium reacts about equally well with fluorene in DME at 22° and at 85° C.

The lithium, sodium and potassium salts of fluorene were all completely dissolved in DME even at room temperature and formed red solutions.

Table IV a

Metalation of Fluorene in 1,2-Dimethoxyethane (b.p. 85° C at 700 mm).

Metal	Temperature of reaction	Observations	Extent of[b] metalation
Li	22°	Small pieces. Complete reaction in ~5 hours. Product soluble at R.T.[a]	80 - 90 %
Li	reflux	Small pieces. Complete reaction in ~5 hours. Product soluble at R.T.	80 - 90 %
Na	22°	Small pieces. Complete reaction in ~8 hours. Product soluble at R.T.	80 - 90 %
Na	reflux	Small pieces. Complete reaction in ~10 hours. Product soluble at R.T.	80 - 90 %
K	22°	Complete in ~2 hours. Product soluble at R.T.	90 - 95 %
K	reflux	Complete within 1 hour. Product soluble at R.T.	90 - 95 %

(a) R.T. = room temperature

(b) Estimated by the methylation technique

Table IV b

Metalation of Fluorene in 1,2-Diethoxyethane
(b.p. 118° C at 700 mm)

Metal	Temperature of reaction	Observations	Extent of metalation
Li	22°	About 20% unreacted after ~ 5 hours. Product largely insoluble at R.T.	--
Li	reflux	Complete reaction in 5-6 hours. Product largely insoluble at R.T.	70 - 80 %
Na	22°	Incomplete in 50 hours.	--
Na	reflux	Nearly complete in ~ 30 hours Product largely soluble at R.T.	70 - 80 %
K	22°	Complete in ~ 3 hours. Product soluble at R.T.	70 - 80 %
K	reflux	Complete in ~ 2 hours. Product soluble at R.T.	70 - 80 %

However, 9-fluorenylpotassium gave an intensely dark red solution, while those of the sodium and lithium compounds were light red in color, the latter being somewhat less intense than the former. Results obtained by the methylation technique indicated that the degree of conversion of fluorene to organometallic product was at least 80 per cent with all three metals. In contrast, with boiling dioxane as solvent, potassium required four hours to be converted to 9-fluorenylpotassium, whereas sodium and lithium reacted very slowly, giving in four hours less than five per cent metalation.

With 1,2-diethoxyethane as solvent (b.p. 118° to 120°/700 mm) potassium again reacted readily at room temperature, the metal disappearing in about three hours. Here again, the exothermic reaction raised the temperature rapidly to the melting point of potassium, hence a cooling bath was required. At reflux temperature, the molten metal appeared to have reacted totally in slightly under two hours. Metallic sodium at room temperature was about 75 per cent consumed in 50 hours, but at the boiling point of DEE only a very small amount of the metal remained after 30 hours. Lithium also reacted slowly at room temperature, being incompletely consumed even after 50 hours. At the boiling point of DEE, where lithium is still solid, complete reaction occurred in 5 to 6 hours - a time not much longer than found for the reaction of lithium in DME. At reflux temperature of the solvent DEE, the fluorenyl salts of lithium, sodium and potassium were all quite soluble, but when the solution was cooled to room

temperature, the lithium compound precipitated largely from solution, while the sodium and potassium compound were nearly completely soluble. The experiments in DEE were repeated several times to check the results and in all three cases for the three metals, where the reaction was apparently complete, the extent of metalation was determined from the methylation technique to be at least 70 to 80 per cent.

In tetrahydrofuran, potassium at room temperature reacted completely in 2.5 hours, lithium completely in 5 hours, but the reaction of sodium was definitely incomplete (not more than 30 %) in 48 hours. In refluxing THF (b.p. 65° /700 mm) potassium disappeared totally within one hour, lithium in 7 to 8 hours while sodium was still incompletely dissolved (about 50 %) in 48 hours. The product from all three metals remained quite soluble in THF both at the boiling point and at room temperature.

It should be pointed out here that the ether solvents used for the metalation experiments were purified by distillation from sodium or potassium metal. This was necessary since Morton et al. (46) had shown that the presence of alkoxides, which would arise from alcohol impurities in the solvent, may influence the metalation reaction. Anhydrous conditions, an obvious requirement for the preparation of organometallic compounds, were maintained by storage of the purified solvents over potassium or sodium wire.

Table IV c

Metalation of Fluorene in Tetrahydrofuran
(b.p. 65° C at 700 mm)

Metal	Temperature of reaction	Observations	Extent of metalation
Li	22°	Little reaction in 4 hours. Complete in 50 hours. Product soluble at R.T.	80 %
Li	reflux	Complete in 7-8 hours. Product soluble at R.T.	80 %
Na	22°	Incomplete in 50 hours Product soluble at R.T.	--
Na	reflux	Incomplete in 48 hours. Product soluble at R.T.	--
K	22°	Complete in 2.5 hours. Product soluble at R.T.	--
K	reflux	Complete in 1 hour.	70 %

g) The Reaction of Potassium Metal with Fluorene in Hydrocarbons Containing DME, DEE or THF .

Since dioxane was found to be a less effective medium for the direct metalation of fluorene than tetrahydrofuran and the ethers of ethylene glycol, when used as pure solvents, the superiority of the latter should also be evident, when diluted with hydrocarbons. It will be recalled that when diluted with hydrocarbons dioxane was found to be superior to ordinary dialkyl ethers, similarly diluted, in promoting the reaction between potassium and fluorene. Thus a twenty per cent dioxane content in hydrocarbons brought about metalation, whereas the presence of twenty per cent of dialkyl ethers in the hydrocarbons showed no better reaction than that found with the pure hydrocarbon solvents. The experiments confirmed this expectation. The results obtained from the metalation experiments in the mixed solvents are compiled in Table V.

The addition of DME, DEE or THF to toluene to the extent of twenty per cent led to a better reaction between fluorene and potassium than had been found for dioxane in toluene. In all cases the organometallic compound largely precipitated from the refluxing solution as a reddish-brown solid, although the intensity of the color of the solution indicated that a considerable amount of the product was still in solution. The order of effectiveness in promoting reaction between fluorene and the metal is apparently DME $>$ DEE $>$ THF $>$ Dioxane, the same order as

Table V

Metalation of Fluorene in Mixed Solvents at Reflux Temperature.

Solvent	Metal	Observation	Extent of metalation (a)
toluene + 20 % dioxane	K	Incomplete in ~ 5 hrs. Product largely insoluble.	40 - 50 %
toluene + 20 % DME	K	Complete in ~ 2 hours Product largely insoluble.	60 - 70 %
toluene + 20 % DEE	K	Nearly complete in ~ 4 hours. Product largely insoluble	60 - 70 %
toluene + 20 % THF	K	Incomplete in ~ 4 hours. Product largely insoluble.	50 - 60 %
dioxane + 10 % DME	Li	Complete in ~10 hours. Product soluble at R.T.	90 %
	Na	Incomplete in ~ 24 hours. Product soluble at R.T.	50 %
	K	Complete in ~ 2 hours. Product soluble at R.T.	90 %
heptane + 20 % DME	K	Complete in ~ 3 hours. Product soluble at R.T.	90 %

(a) Estimated by reaction with methyl iodide and examination of the product.

found when the ethers indicated were used as solvents in pure state. Whereas 5 hours of reflux in toluene-dioxane mixture gave about 50 per cent metalation of fluorene by potassium, the DME-toluene mixture, after 2 hours reflux, brought about apparently complete disappearance of the potassium. Also no unreacted potassium was detected when methyl iodide was added subsequently in the step which tested for the extent of metalation. But since only 60 to 70 per cent methylation was found, either the 9-fluorenylpotassium failed to react with all the methyl iodide, which is an unlikely event in view of the facile reaction experienced in analogous cases, or the remaining unreacted potassium was occluded by the precipitate in a sufficiently finely divided state so as to avoid detection. A 20 per cent solution of DEE or THF in toluene, kept at reflux for 4 hours, gave obviously incomplete reaction between fluorene and potassium since upon methylation unreacted metal was detected. The extent of methylation in DEE-toluene was 60 - 70 per cent, about that found for the 2 hours reaction in DME-toluene. About 50 per cent of methylated fluorene was isolated from the corresponding reaction in THF-toluene. Thus the reaction of potassium with fluorene in these mixed solvents was best with DME and DEE as cosolvents and somewhat less with THF as cosolvent. The addition to toluene of even one per cent DME was sufficient to cause improved reaction between fluorene and potassium, whereas such a small amount of dioxane had been found to be ineffective.

It was interesting that a refluxing solution of 20 per cent DME in heptane gave complete reaction of fluorene with

the added potassium in only 3 hours. Here, however, the solid 9-fluorenylpotassium did not precipitate, but instead, two layers were formed. The nearly colorless upper layer, composed of heptane and some DME, and the lower dark red layer, containing the 9-fluorenylpotassium and DME, contaminated by some heptane. The same observation was made when a DME solution of the salt, prepared in pure DME, was diluted strongly with heptane. This and other experiments concerning the solubility of the alkali metal derivatives of fluorene will be reported in the following section.

h) The Participation of the Ether Solvents in the Formation of Alkali Metal Salts of Fluorene.

The observation, made throughout these metalation studies, can be rationalized on the basis of four concepts: 1. The greater ionization potential of sodium and lithium compared with that of potassium. 2. The greater ionic character of the potassium-carbon bond as compared with that of the sodium-carbon or lithium-carbon bond. 3. The smaller ionic radius of lithium as compared to that of sodium. 4. The availability of the unshared electrons of the ether oxygen for the solvation of the metal ion.

It is expected and actually observed (47) that the reaction of metallic sodium with organic halides to form the organometallic product be quite facile, since the carbon-halogen bond in the halides possesses considerable polar character.

In contrast, the C-H bond at carbon 9 of fluorene has very little polar character. The low acidity of fluorene (4, 5) is in agreement with this view. Hence it is clear that a more electropositive metal, potassium rather than sodium and lithium, will be more effective under any conditions in converting fluorene to the organometallic compound. The hydrogen atom, thus replaced, is subsequently eliminated as hydrogen gas. For the same reason potassium was the only metal which gave any significant reaction with fluorene at all in alkyl ether and in dioxane. Accordingly rhubidium and cesium should be more effective than was potassium. Indeed, cesium has been found to metalate even an extremely weak acid such as toluene (48).

Since there is definitely a reaction between metallic sodium and fluorene in dioxane solvent, as shown by the reddish-brown deposit on the surface of the metal and by actual isolation of 9-substituted fluorene in small yields (less than 5 %), the electropositivity of sodium metal must be sufficient to cause at least a slow reaction. But as the reaction is quite obviously limited, an important aspect of the reaction must be solvation of the product, or of the positive ion at the stage of the reaction where the metalorganic compound just begins to form. The solvation must occur with much difficulty in the case of 9-fluorenylsodium in dioxane. This view is supported by the observation that in the case of the reaction with potassium and fluorene in dioxane the color due to the fluorenyl anion, or to

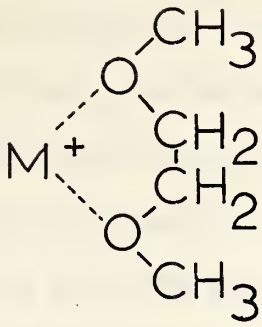
the ion pair formed by coordination of this anion with the potassium ion, reaches a maximum and is quite intense within a few minutes of the beginning of the reaction. Further formation of 9-fluorenylpotassium occurs with simultaneous deposition of the compound as a solid from the saturated solution. In contrast, even a reaction time of 4 hours with sodium and fluorene in dioxane, giving less than 5 per cent reaction, produces very little color in solution. In dimethoxyethane and tetrahydrofuran, where no precipitation of the metal salts occurs, the color deepens gradually as the reaction proceeds.

When solid 9-fluorenylpotassium or 9-fluorenyllithium was suspended in dry pentane or hexane the liquid remained colorless. This lack of solubility is also in accord with the failure of the metals to undergo any significant reaction with fluorene in these solvents and again emphasizes the importance of solvation.

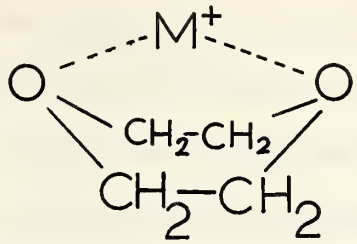
The indications are that in dioxane, even though lithium is less electropositive than is sodium, it reacts with fluorene nearly as readily as does sodium, a situation not expected in view of the much greater rate of reaction shown by potassium over that of sodium and the difference in electropositivity of the three metals. The combined solvation effect of the ether and the electropositivity of the metal determine the reaction of the metal.

Accordingly the lithium ion must be more readily solvated by ethers than is the sodium ion, probably due to its smaller ionic radius which permits a closer approach to the favorably located and exposed oxygen atoms in the ethers. Thus the lower electron releasing ability of lithium is in part compensated by the greater facility of the metal ion to participate in solvation or complex formation in the presence of dioxane. In the solvents with greater coordination power, such as DME, DEE and THF, this tendency is even more pronounced and thus places lithium ahead of sodium in respect to the reactivity toward fluorene.

It is clear from the preparation of the lithium, sodium and potassium salts of fluorene that the solvents of choice are, in order of effectiveness, DME > DEE > THF > dioxane > dialkyl ethers. The presence of two oxygen atoms in a molecule of solvent combined with an easily attainable conformation, which is favorable for solvation, places DME in the first place. Dioxane requires the less favored boat form for solvation according to the same principle, hence is considerably less effective as a solvent for this reaction. Figures A and B illustrate the coordination of the metal ion with dimethoxyethane and dioxane respectively.



A



B

At its boiling point and under the influence of the potassium ion dioxane may be capable of existing to a noticeable extent in the boat form, although the chair form is reported to be the predominant one under ordinary conditions (49) since its dipole moment is practically zero (50).

The larger bulk of the ethyl group in 1,2-diethoxyethane offers some steric hindrance to the coordination and makes DEE slightly less effective than DME. The high effectiveness of tetrahydrofuran, although it possesses only one oxygen atom per molecule, may be explained by the greater exposure of oxygen due to the five-membered ring structure.

The solvation ability of these ethers is in the same order as the efficiency of the solvents in promoting metalation reactions. This was tested by attempts to remove the solvent from the metal salts of fluorene. The 9-fluorenylpotassium, prepared in dioxane, was separated from the dioxane solvent, washed with hexane and then analyzed by infrared spectroscopy in

a nujol mull for ether content. No evidence for ether oxygen was found. The hexane wash obviously quite readily removed the ether from this complex. This is also in accord with the observation that dioxane solutions of 9-fluorenylpotassium upon strong dilution with hexane had been found to precipitate most of the salt. However, with DME as the solvent, the added hexane competed with the metalated fluorene for the DME far less effectively than it had competed with the 9-fluorenylpotassium for dioxane. No solid metal salt precipitated but two liquid layers were formed, an upper layer of hexane and a dark red lower layer containing 9-fluorenylpotassium and DME. Frequent washings with hexane failed to remove DME from the metalorganic compound, which remained liquid and showed definitely the presence of ether oxygen in the infrared spectrum.

Since hexane was unable to remove the strongly associated DME from the organometallic compound , it was thought that a solvent more compatible with DME than was the hexane might be more effective. The choice of such solvents was limited to those which themselves did not dissolve the salt readily. Accordingly diethyl ether was mixed with this red layer and allowed to stand at room temperature . A brown precipitate did appear, but its oily nature prevented crystallization from occurring. Cooling the hexane-diluted or ether-diluted DME solution to zero degrees was of no advantage.

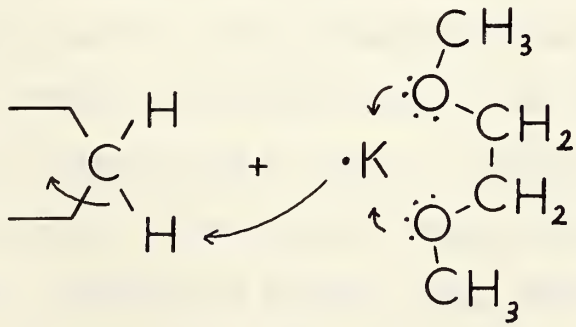
The 9-fluorenylsodium prepared in DME behaved as did the 9-fluorenylpotassium. DME, containing 9-fluorenyllithium, when diluted with hexane also gave a lower red layer of the ether-organometallic complex which also failed to precipitate any solid at first. However when this solution was poured into a large excess of hexane solid 9-fluorenyllithium precipitated. Addition of the original DME solution of the lithium salt to dioxane failed to precipitate a salt or to form a second layer. Addition of the DME solution of 9-fluorenyllithium to toluene gave at first only a single phase red solution but soon a red solid precipitated slowly. When a portion of the original DME solution of the 9-fluorenyllithium was poured into excess diethyl ether a red precipitate of the lithium salt readily occurred, although some remained in solution as judged by the red color.

i) The Mechanism of the Metalation by Alkali Metals.

Since the experiments had clearly shown that solvation is an essential requirement for a successful reaction between alkali metals and fluorene, there remained the question whether : 1. Solution of traces of alkali metal occurs prior to reaction, 2. The solvent participates in the actual reaction of the metal with fluorene, 3. The action of the solvent is to remove the resulting organometallic compound from the surface of the metal and thus permit further reaction.

permit further reaction.

A number of studies concerning the solution of alkali metals in ethers (44, 45) point out that potassium will dissolve in certain favorable ethers such as the 1,2-dimethoxyethane, to give blue, electrically conducting solutions. The same report states that no solution of potassium is observed in dialkyl ethers or dioxane. Apparently no solution whatsoever occurs with sodium or lithium, even in the most favourable ethers. If this holds true for the ethers under investigation in this work at reflux temperature, then the requirement of solution of the metal before it can react would place potassium in the same category as lithium or sodium. However, the incipient solution of potassium should be greater than that of lithium or sodium and the presence of an electron acceptor such as fluorene would supply the necessary feature for the reaction when promoted by the solvating effect of the ethers as illustrated:



However, that the metal must first dissolve in the ether before it reacts with fluorene is rather unlikely, not only because Down et al. (44) has found that the solubility of

the metal in ethers increases with decreasing temperature, (although this may not be true when one works at elevated temperatures, such as employed for the metalation reaction) but also considering the very small amounts of metal (10^{-3} mol/l), found to dissolve in the ethers (44, 45) in comparison with the high velocity of metalation which was observed in some cases of the present work. Kharasch (41) has expressed the view that the prime effect of the solvent in promoting the formation of Grignard reagents is that of solution of the organometal with the consequent exposure of a clean surface of the metal to the organic halide. The results obtained in the present work, however, suggest that the solvent actually participates in the formation of the metalorganic compound and thus is part of the reaction process. Reaction is hastened, no doubt, by exposure of a clean metal surface via more facile removal of the organometallic compound from this surface due to improved solvation of the product. The solid, dioxane-free 9-fluorenylpotassium, suspended (and insoluble) in heptane is quite definitely deeply colored. The fact that even the very reactive molten potassium shows no coloration of the bright surface of the metal when it is refluxed with fluorene in heptane, indicates that there is actually no 9-fluorenylpotassium coating on the surface of the metal, thus preventing further reaction. Addition of dioxane, DME, DEE or THF to this heptane supplies the type of solvent necessary to participate in the formation of 9-fluorenylpotassium as well as to remove this

product from the metal surface.

Solid 9-fluorenyllithium, made in DEE, dissolves readily in dioxane, but the reaction of lithium and fluorene in dioxane was found to be very slow, if not negligible. In refluxing dioxane after a period of 15 hours, lithium and fluorene gave only very little reaction. This reveals that the removal of the product from the surface then, cannot be the important factor, and gives further support to the view that the ether participates in the formation of the metal organic compound.

3. Effect of Ether Solvents in Some Related Reactions.

a) The Metalation of Fluorene by Sodium- and Lithium Amide.

The method for the preparation of 9-fluorenylsodium from the reaction of fluorene with powdered sodamide in boiling decalin (19) in our hands, did not produce the desired salt as a crystalline compound, but instead formed a tarry material which could not be readily isolated and freed from the high boiling solvent. It was thought that the replacement of decalin by dioxane might improve this reaction since dioxane has been found to be a favorable medium for the preparation of isolatable solid 9-fluorenylpotassium. The solid 9-fluorenylsodium was desired especially for the alkylation experiments in hydrocarbon solvents.

Isolation of the solid 9-fluorenylsodium from the reaction of sodium with fluorene in 1,2-dimethoxyethane, 1,2-diethoxyethane and tetrahydrofuran had not been successful in spite of the facility of the reaction under such conditions, since the sodium salt was quite soluble in these solvents and hence failed to precipitate even upon dilution of these solvents with hexane. The direct reaction between sodium and fluorene in boiling dioxane was also quite unsatisfactory as reported in a preceding section, although, in this medium the salt is largely insoluble. However, refluxing a mixture of fluorene, powdered sodamide and

dioxane for a period of time was quite successful. The same reddish brown precipitate occurred as in the case of the potassium compound. The 9-fluorenylsodium which formed could be separated readily from dioxane but the unreacted sodamide was also retained as a contaminant. Under these conditions metalation had occurred to at least 60 per cent as determined from the yield of methylated fluorene, obtained by addition of methyl iodide to the 9-fluorenylsodium. In dimethoxyethane sodamide reacted even more readily with fluorene. In three hours 0.05 moles of a good grade of sodamide reacted apparently completely with an equivalent amount of fluorene in the refluxing solvent, as compared to ten hours required for the reaction of 0.05 gramatoms of sodium metal under the same conditions. The extent of metalation was again measured by methylation and found to be 70 per cent. Thus 9-fluorenylsodium of good quality can be prepared more readily using sodamide, rather than metallic sodium. However, the presence of contaminating unreacted sodamide may in some instances be troublesome.

To round out the investigation lithium amide was tested. Although a technical grade of this reagent was used, it reacted apparently completely in five hours to yield 60 per cent metalation as determined by the methylation technique. The clear solution of the organometallic compound in dimethoxyethane obtained in this manner possessed a deeper red color than those obtained by the direct action of the metal with fluorene. This may be due to the presence of ammonia since the addition of dry gaseous ammonia

to the 9-fluorenylsodium prepared from sodium metal reacting with fluorene in dimethoxyethane, actually caused intensification of the color. Thus 9-fluorenyllithium may also be prepared from lithium amide and fluorene. However, due to the presence of contaminating unreacted lithium amide, this method is much inferior to the direct metalation of fluorene by lithium metal since the latter proceeded readily in the aforementioned ethers of ethylene glycol.

b) The Reaction of Triphenylmethane and Diphenylmethane with Lithium, Sodium or Potassium in Dimethoxyethane as Solvent.

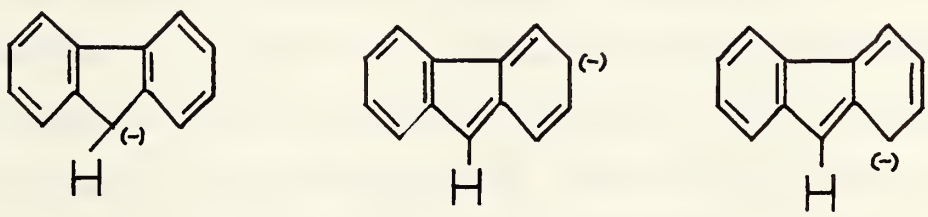
Triphenylmethane was found to react with potassium, showing the red color characteristic of the metal salt after 30 minutes of reflux. The metal was completely consumed in 10 hours. Reaction of the organometallic compound with benzyl chloride gave the expected 1,1,1,2-tetraphenylethane in good yield. Both sodium and lithium under the same conditions reacted very slowly with triphenylmethane and in a period of 100 hours had reacted only to the extent of about 10 per cent as judged by the weight of the unreacted metal. Diphenylmethane after three days reflux in dimethoxyethane had consumed nearly all potassium. Lithium under the same conditions in 30 hours showed only a slight accumulation of red solid on the surface of the metal but no solution of the product.

c) The "Dimetalation" of Fluorene.

Since all potassium metal appeared to be consumed when two equivalents of potassium metal were allowed to react with one equivalent of fluorene in refluxing dioxane, and furthermore yields up to 65 per cent of 9,9-disubstituted fluorenes were obtained from the reaction of the resulting metalated fluorene with alkyl halides, it was at first thought that a dipotassium compound must have formed under these conditions. This view was further supported by results from deuteration experiments, where almost completely dideuterated fluorene was obtained, when the "dipotassium salt" was treated with an excess of D_2O. The bands on the infrared spectrum assigned for the CH_2 group were eliminated completely, whereas the bands for the CHD group were strongly reduced in intensity (Fig. 3). No change in extent of deuteration was found when a greater proportion of potassium metal was employed.

The high instability of the "dipotassium compound", experienced when attempts were made to free it from dioxane solvent, also seemed to point to a material different from 9-fluorenylpotassium, since the latter could be readily freed from dioxane solvent without much decomposition. The view of the existence of a dipotassium salt of fluorene is not unreasonable, since Huckel (22) reported that a disodium compound of fluorene was formed by addition of two sodium atoms to each fluorene molecule in liquid ammonia. This material yielded dihydrogenated

fluorenes rather than ordinary derivatives of fluorene upon subsequent reactions with ammonium chloride or methyl iodide. Furthermore the recent work of Hauser (26) showed the existence of dicarbanions, formed from the reaction of dibenzyl ketone or dibenzyl sulfone with two equivalents of potassium amide in liquid ammonia. However, these dicarbanions were highly resonance stabilized by neighboring C = O or C ≡ N groups, a situation not existing in fluorene, although the monocarbanion of fluorene is considered to be stabilized to some extent (27, 51, 52) by contributing structures such as:



Since it is rather unlikely (22), that the two negative charges in the "dipotassium fluorenyl" are located at the C_9 position, one would assume one negative charge to be at C_9 which is undoubtedly the most acidic position in the fluorene molecule, but the second charge at some position in the ring. This situation would parallel the dimetalation of toluene as reported by Morton et al. (53) and others, where at first lateral metalation occurred followed by metalation on the aromatic ring in meta position to the methyl group. That the subsequent reaction of the dipotassiofluorene places both substituents at C_9 rather than

at the positions where the metals were located, has already been reported and rationalized by Huckel (22).

In the present case, the formation of a dipotassiofluorene could not be confirmed as shown by a number of experiments. All attempts to increase the yields of the alkylated fluorene above 65 per cent from the reaction of the "dipotassiofluorene" in dioxane with alkyl halides have met with consistent failure. Further investigations have shown that the first atom of potassium reacted with fluorene to produce 9-fluorenylpotassium and an equivalent amount of hydrogen. Treatment of the 9-fluorenylpotassium, so formed, with a second equivalent of potassium metal in dioxane evolved no hydrogen. The metal, finely dispersed in the precipitated 9-fluorenylpotassium, could not be readily perceived as unreacted metal. But the reaction of two equivalents of potassium metal with one equivalent of fluorene in dimethoxyethane gave a red solution of 9-fluorenylpotassium. Under these conditions the second equivalent of potassium remained unreacted and could be clearly seen suspended in the solvent. Thus in the case of dioxane solvent the second equivalent of potassium must have been occluded by the brown precipitate, thus evading detection.

The existence of the second equivalent of potassium as unreacted metal which would then react competitively with the alkyl halide and with monoalkylated product, probably more rapidly with the former than with the latter, would thus account for the

inability to increase the yield of alkylated fluorenes over 65 per cent.

It should be mentioned here, that the monopotassium salt of fluorene itself can account for up to 40 per cent of disubstitution under these conditions, as will be reported later. The additional amount must be produced by either further metalation by unreacted potassium metal as outlined obove, or by the actual existence of a small amount of dipotassiofluorene along with the monopotassium salt, the bulk of the second equivalent of potassium remaining unreacted. This situation would parallel several reports in the literature, where the extent of dimetalation is usually quite small (54). The formation of any substantial amount of dipotassiofluorene is not supported by the analysis of the amount of hydrogen produced.

4. The Reaction of Alkali Metal Derivatives of Fluorene with Alkyl Halides.

The reaction of a monometalated organic compound with an equimolar amount of alkyl halide would be expected to yield the corresponding monoalkyl derivative of the anion involved. However, using methylation by methyl iodide as a means to determine the extent of metalation of fluorene by potassium metal, followed by chromatographic separation of the product, revealed at a very early stage of this work that not only 9-methylfluorene, but also 9,9-dimethylfluorene had definitely been produced. This finding was especially interesting since no report had been found in the literature that alkylation of fluorene using equimolar amounts of reagents resulted in the formation of disubstituted derivatives.

Greenhow (19), who treated various alkyl halides with 9-fluorenylsodium in petroleum ether, reported only monoalkylated fluorenes as products. Hence, either the solvent or the particular metal substituent or both must be responsible for the production of disubstituted derivatives. From the present work it appears that the phenomenon of disubstitution accompanying the expected monosubstitution is quite general with the alkali metal derivatives of fluorene.

a) The Reaction of 9-Fluorenylpotassium with Alkyl and Aralkyl Halides.

The 9-fluorenylpotassium, made in dioxane solvent from equimolar amounts of fluorene and potassium metal, was treated in the same solvent with a number of alkyl halides. As was pointed out previously a large part of the potassium salt precipitated from the solution when cooled from reflux- to room temperature, but nevertheless a considerable amount appeared to remain in solution as judged by the dark color of the latter. The reaction with all alkyl halides investigated, methyl iodide, ethyl bromide, benzyl chloride and allyl bromide, occurred quite readily with evolution of heat; therefore it was necessary to add the halides slowly to the solution or suspension of the metal-organic compound and a cooling bath was required.

Usually a sample of the reaction product was separated on a chromatographic column, packed with alumina. The elution was performed with hexane or pentane solvent. The first compound emerging from the column in case of the methyl derivatives was the 9,9-dimethylfluorene, followed by 9-methylfluorene and finally by fluorene. The same order of elution occurred with the ethyl- and allyl derivatives. By this procedure it was possible to determine the relative amounts of di-, mono- and unsubstituted fluorene present in the reaction mixture.

In the case of methylation of the 9-fluorenylpotassium in dioxane it was found that 26 per cent of the fluorene was converted into dimethylfluorene, 43 per cent into the monomethylfluorene and 31 per cent remained unreacted. Repetition of the experiment gave essentially the same proportion of mono- and disubstituted material. Since the acidity of the substituted fluorene might be an important factor in determining the extent of disubstitution, as will be pointed out later in the discussion of these results, the effect of the size and nature of the substituent at C_9 of fluorene was investigated.

The reaction of ethyl bromide and 9-fluorenylpotassium in dioxane was found to produce 27 per cent of 9,9-diethylfluorene, which is an increase of only one per cent over the results found for the methylation reaction. Since this is within the experimental error it is considered as insignificant in regard to the discussion of any substituent effect. The reaction with allyl bromide did not reveal any effect of the substituent either. Again 27 per cent of the fluorene was converted into diallylfluorene and 40 per cent into monoallylfluorene, the drop of three per cent of the yield of monosubstitution again being too small bo be of significance. Such small deviation may be caused by errors in evaluation of the infrared spectra of the fractions obtained from the chromatographic column, or may arise from differences in the rates of addition of the reagents to the 9-fluorenylpotassium and the efficiency of the stirring from one

reaction to another. Attempts were made at all the times to keep such conditions as uniform as possible.

The reaction of 9-fluorenylpotassium and benzyl chloride in dioxane likewise occurred very readily and resulted in 23 per cent of dibenzylation. However, this figure may be lower than the actual amount of disubstitution produced, because the dibenzylfluorene had to be separated from monobenzylfluorene and unreacted fluorene by crystallization technique, since no solvent could be found to separate this particular mixture satisfactorily on a chromatographic column. Pentane, hexane and heptane did not elute the dibenzylfluorene and separated monobenzylfluorene from fluorene only very poorly, whereas mixtures of benzene with those solvents did elute dibenzylfluorene but did not separate monobenzylfluorene and fluorene at all. The same was found when methanol or ethanol or their mixtures with aliphatic hydrocarbon solvents were used as eluents. For this reason the amount of monobenzylfluorene obtained from the reaction of 9-fluorenylpotassium and benzyl chloride could not be estimated, since fluorene and monobenzylfluorene could not be separated satisfactorily enough to justify a statement about their relative amounts present in the product.

As an overall result it may be stated that the amount of disubstituted material obtained from the reaction of potassium fluorenyl and alkyl halides in <u>dioxane</u> was about 25 - 30 per cent of the fluorene originally used to form the

potassium compound and fell somewhat short of equivalence to the amount of unchanged fluorene. This extra quantity of fluorene most likely is that which had originally failed to react with the metal. From the examination of the results of alkylation in dioxane solvent it was found that the ratio of disubstitution to monosubstitution appears to be independent of the size of the alkyl or aralkyl groups used. The relative yields obtained in the various experiments are summarized in Table VI.

Greenhow (19) did not report any disubstituted material from the reaction of 9-fluorenylsodium and alkyl halides in petroleum ether solvent, a result which could be confirmed in course of this work. It was interesting therefore to note that the same reaction performed with potassium fluorenyl under otherwise identical conditions yielded a somewhat different result. The 9-fluorenylpotassium made in dioxane could be completely precipitated by addition of an excess of aliphatic hydrocarbon solvents. This precipitate, washed twice with heptane or hexane by suspension in the solvent and decantation of the liquid after the precipitate had settled, was suspended in the hydrocarbon solvent and allowed to react with the chosen alkyl halide. One notable difference between the reaction with 9-fluorenylpotassium and alkyl halide in dioxane and the same reaction in hydrocarbon solvents was the rate of reaction. Whereas in dioxane nearly all the solid suspension of the reddish-brown 9-fluorenylpotassium had disappeared within a few minutes, the same reaction in heptane showed some unreacted brown material

even after an interval of 30 minutes. The marked difference in the rate of reaction is no doubt due to the partial solution of the 9-fluorenylpotassium which occurs in the ether but not in aliphatic hydrocarbons. This was born out by the observation that the depth of the reddish color of the ether solution could be correlated, if only roughly, with the rate of reaction when, for the experiments concerned, equivalent quantities of reagents were used. No color was observed in the solvent for the heptane suspension, hence in this medium the reaction with the alkyl halides is considered to occur heterogeneously on the surface of the suspended solid, resulting in a much slower reaction dependent in part upon diffusion rate and efficiency of stirring.

The reactions of 9-fluorenylpotassium, suspended in aliphatic hydrocarbon solvent, with an equimolar proportion of methyl iodide and benzyl chloride were investigated. In both cases the amount of fluorene which was converted into the disubstituted product was found to be around 5 per cent, while the amount of monosubstituted fluorene, actually isolated in case of methylfluorene, was 75 - 85 per cent. The remainder of the product was unchanged fluorene. Again one should keep in mind that the 5 per cent disubstitution obtained for the methylation can be considered as reasonably accurate, since a sample of this product was separated on the chromatographic column. On the other hand the dibenzylfluorene was separated from monobenzylfluorene and fluorene by preferential extraction of the latter two compounds using

Table VI

Conversion of Fluorene into Mono- and Disubstituted Derivatives by Reaction of 9-Fluorenylpotassium with Various Alkyl Halides in Dioxane Solvent.

Alkyl halide	Disubstitution %	Monosubstitution %	Fluorene %
Methyl iodide	26	43	31
Ethyl bromide	27	43	30
Allyl bromide	27	40	33
Benzyl chloride	23	(a)	(a)

(a) Accurate amounts unknown since quantitative separation of the monobenzylfluorene from fluorene was not achieved.

petroleum ether or cold alcohol, a procedure which left the much less soluble dibenzylfluorene. Since some of the dibenzylfluorene may have dissolved in the cold solvent and could not be recovered by fractional crystallization, there may have been actually somewhat more than 5 per cent of dibenzylfluorene in the original product.

The benzylation was also performed in diethyl ether as solvent. The 9-fluorenylpotassium, made in dioxane and freed from this solvent by hexane using the technique as outlined before, was suspended in ethyl ether. The solvent became reddish colored, indicating that a small part of the organometallic compound was in solution. The addition of benzyl chloride and working up the mixture as usual indicated that 25 per cent of the fluorene had become 9,9-dibenzylfluorene.

Since dioxane and diethyl ether gave rise to substantial disubstitution while hydrocarbons produced essentially monosubstitution, a number of other solvents were then investigated to determine their influence on the course of the reaction. Table VII shows a summary of the reactions between methyl iodide and 9-fluorenylpotassium in these solvents. The reaction in 1,2-dimethoxyethane (DME), the solvent which had been found to be much superior to dioxane in promoting the metalation, and in which all the 9-fluorenylpotassium remained in solution, dark red in color, caused a larger proportion of disubstitution to occur than did dioxane.

Table VII

Products of the Reaction of 9-Fluorenylpotassium with Methyl Iodide in Various Solvents.

Solvent	Time[d]	Dimethyl-fluorene %	Monomethyl-fluorene %	Fluorene %
DME	1 hr.	35	30	35
DEE	1-2 hrs.	25	22	53
THF	4 hrs.	20	20	60
Dioxane	4 hrs.	25	40	35
Toluene-DME[a]	4 hrs.	20	20	60
Toluene-DEE[a]	4 hrs.	--	--	--
Toluene-THF[a]	4 hrs.	10	25	65
Toluene-dioxane[a]	4 hrs.	5	40	55
Heptane-DME[a,b]	3 hrs.	33	30	37
Heptane or Hexane[c]	4 hrs.	7	40	53

(a) The ratio of ether to toluene was 4:1 by volume.

(b) Two layers were formed during the reaction (see text).

(c) The 9-fluorenylpotassium was prepared in dioxane, isolated, and then suspended in the hydrocarbon solvent for reaction with methyl iodide.

(d) The time allowed for the formation of the organometallic compound at reflux temperature of the solution.

Since no unreacted potassium was visible in the original clear solution of the potassium fluorenyl, the amount of unreacted fluorene was considered to be small. The results show that 35 per cent of the original fluorene became disubstituted, an equal amount of unreacted fluorene was found, and the remainder was 9-methylfluorene. Thus the use of DME solvent led to an amount of 9,9-dimethylfluorene somewhat greater than that for 9-methylfluorene.

When the reaction was performed in 1,2-diethoxyethane (DEE), wherein the 9-fluorenylpotassium also could be prepared very readily, a greater proportion of unreacted fluorene occurred than was the case with DME, but here again the amount of 9,9-dimethylfluorene slightly exceeded that of 9-methylfluorene, the relative amounts being 25 and 22 per cent respectively. In tetrahydrofuran (THF) equal quantities of mono- and dimethylated fluorene were obtained, the total amount being 20 per cent of each, but 60 per cent of the product emerged as unchanged fluorene.

The efficiency of promoting conversion to the dimethylated product is thus, in decreasing order:
DME $>$ DEE $>$ THF $>$ dioxane. It should be noted that this is the same solvent order as found for the efficiency of the solvents in promoting the direct metalation of fluorene by alkali metals.

The use of mixed solvents or of hydrocarbon solvents alone generally lowered the dimethylation. DME-toluene solvent still gave 20 per cent mono- and 20 per cent dimethyl-

fluorene. THF-toluene gave 10 per cent di- and 25 per cent monomethylfluorene. Toluene-dioxane produced 5 per cent di- and 40 per cent monomethylfluorene, while with heptane alone as the solvent the proportions of di- and monosubstituted fluorenes also were 5 per cent and 40 per cent respectively. In the latter case the 9-fluorenylpotassium had been prepared beforehand in dioxane, which was then replaced by the hydrocarbon solvent for the subsequent reaction with methyl iodide. For the reaction of the organometallic compound in the mixed ether-hydrocarbon solvents the preparation of the 9-fluorenylpotassium was accomplished in the same medium as was used for the reaction of the organometallic compound with the alkyl halide. The results obtained from the methylation of 9-fluorenylpotassium made in heptane-DME mixture and treated with methyl iodide in the same solvent must be considered as an exception. Here the same amount of di- and monomethylation was obtained as found for DME alone. This, however, is reasonable in the light of the aforementioned observations that, when the metal had reacted with fluorene in this solution, two liquid layers soon formed, the lower being essentially the ether, containing 9-fluorenylpotassium, while the upper was essentially heptane, containing some of the ether. Hence the lower layer, where the subsequent reaction occurred, approximated the conditions which held in the case when the solvent was DME only.

b) The Reaction of 9-Fluorenylsodium with Alkyl Halides.

As previously stated, no disubstitution occurred when 9-fluorenylsodium was treated with alkyl halides in aliphatic hydrocarbon solvents. However, when 9-fluorenylsodium, made from sodium amide and fluorene in refluxing dioxane, was left in the same solvent and allowed to react with an equimolar amount of alkyl halide, a different picture resulted. As much as 16 per cent of 9,9-disubstituted fluorene, based on the original amount of fluorene employed, was obtained when the halide was benzyl chloride, while about 10 per cent disubstitution occurred when methyl iodide was the reagent. These results suggest that the benzyl group does produce a greater amount of disubstitution in case of the sodium derivative. The fact that the relationship of the nature of the C_9 substituent and the ratio of di- to monosubstitution was not revealed by the experiments dealing with the potassium compound is quite understandable since the potassium compound is more reactive than the sodium compound and hence less selective in its reactions.

When 9-fluorenylsodium was prepared by direct reaction of the metal with fluorene in 1,2-dimethoxyethane and the salt, completely dissolved in this solvent, then treated with methyl iodide, the same ratio of di- to monosubstitution occurred as had been found for the potassium analogue, namely 35 per cent and 30 per cent respectively. A similar reaction, performed in

diethoxyethane, gave 20 per cent di- and 40 per cent monosubstitution. Since the direct reaction of fluorene with sodium in tetrahydrofuran was very slow a reaction similar to those in DEE and DME was not conveniently accomplished.

It is quite clear that 9-fluorenylsodium reacting with an equivalent amount of alkyl or aralkyl halide does actually produce a considerable quantity of disubstituted fluorene when the decomposition of the salt occurs in ether solvents, particularly the ethers of ethylene glycol. Here again most disubstitution occurred in DME, the solvent found to be most effective for the formation of the salt from the metal and for its ability to dissolve the organometallic compound. For such disubstitution DEE, dioxane and aliphatic hydrocarbons showed decreasing ability in the order stated. In hydrocarbons practically no disubstitution occurred at all. Table VIII summarizes the yields obtained from the reactions of 9-fluorenylsodium with methyl iodide in a number of different solvents.

c) The Reaction of 9-Fluorenyllithium with Alkyl Halides.

The compound 9-fluorenyllithium, which could be conveniently prepared and isolated as a solid material when DEE was used as a solvent for the metalation reaction, was washed with hexane and allowed to react in hexane suspension with an equimolar amount of methyl iodide. No disubstitution seemed to occur under these conditions since practically no dimethylfluorene

Table VIII

Products of the Reaction of 9-Fluorenylsodium with Methyl Iodide in Various Solvents.

Reagent	Solvent	Time[a] (hrs.)	Dimethyl-fluorene (%)	Monomethyl-fluorene (%)	Fluorene (%)
Na	DME	36	35	30	35
Na	DEE	40-50	20	40	40
Na	THF	48	(b)	--	--
Na	dioxane	36	(c)	--	--
$NaNH_2$	DME	3	15	40	45
$NaNH_2$	dioxane	3	10	35	55

(a) Time allotted for the reaction between the metal or amide and fluorene in the refluxing solvents.

(b) The metalation with sodium metal was incomplete in all cases.

(c) The extent of metalation was too small for separation of any product.

was isolated from the product. A yield of 80 per cent of 9-methylfluorene was obtained. When 9-fluorenyllithium was prepared in DME, or DEE and left in these solvents (partly or completely dissolved) for the subsequent reaction with methyl iodide, about 5 per cent of the dimethylfluorene was found in the product, which otherwise consisted largely of monomethylfluorene. The yield of the latter was 80 per cent in case of DME, and 60 per cent in case of DEE. These figures, however, were less accurate than those reported in other cases where the yield was over 5 per cent because quite small amounts of one compound in a very large excess of another were very difficult to estimate from the infrared spectra of the fractions.

It is noteworthy that, when benzyl chloride reacted with 9-fluorenyllithium in DME, disubstitution did in fact occur to an extent of 8 per cent. Even in hexane the benzyl chloride and 9-fluorenyllithium gave a small amount of dibenzylfluorene, though less than 5 per cent. This again indicated that the nature of the substituent may influence the amount of the disubstituted material formed. The fact that the 9-fluorenyllithium showed even better discrimination than did the sodium derivative, may be rationalized by the lower reactivity of the former. The products obtained in the various experiments are compiled in Table IX.

Table IX

Products from the Reaction of 9-Fluorenyllithium with Methyl Iodide in Various Solvents.

Solvent	Time[a] (hrs.)	Dimethyl-fluorene (%)	Monomethyl-fluorene (%)	Fluorene (%)
DME	4-5	5	80-85	10-15
DEE	5-6	5	60	35
THF	8	1-2	85	4-13
Hexane[b]	--	0	80	20

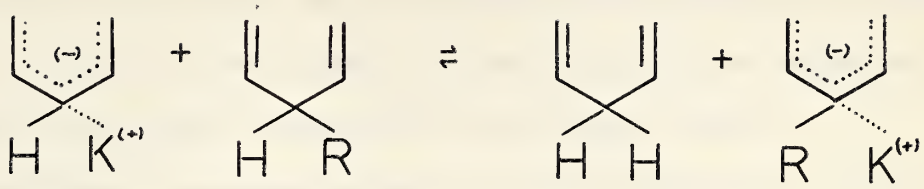
(a) Time allotted for the formation of the organometallic compound in the refluxing solvent.

(b) 9-Fluorenyllithium was prepared in DEE, then isolated, suspended in hexane and treated with methyl iodide.

d) The Effect of Solvents and Nature of the Metal on the Ratios of Mono- to Disubstitution produced in the Reactions of the Alkali Metal Salts of Fluorene and Organic Halides.

The results obtained from the reactions of 9-fluorenyllithium, -sodium or -potassium can be rationalized on the basis of a) the insolubility of the organometallic compound in hydrocarbons like heptane or hexane, but its solubility, though limited in some cases, in ethers; b) the relative electropositive nature of the three metals thus giving rise to both the ionic character and reactivity of the carbon-metal bond in fluorene in the order K-C $>$ Na-C $>$ Li-C; c) the acidity of fluorene and C_9-monosubstituted fluorenes.

In nonpolar and non-ionizing solvents such as hexane, all three alkali metal fluorenyls posses closely associated cations and anions having a considerable amount of covalent character in the metal-carbon bond. The reaction with the organic halide in hexane occurs by the attack at the surface of the insoluble and suspended solid. The more polar C-K bond should react with the organic halide more quickly than does the C-Li bond. The monosubstituted fluorene, as soon as it is formed, can escape from the surface of the solid into solution. However, if the newly formed 9-monosubstituted fluorene possesses an acidic hydrogen, there will occur on the surface of the solid a reaction between the product and more of the salt, as shown below.



The position of this equilibrium will depend upon the acidity of the monosubstituted fluorene. This would lead to disubstitution after further reaction with more of the alkyl halide. Since little or no disubstitution occurred in the reaction of 9-fluorenyllithium, and very little 9,9-disubstituted fluorene was formed when the potassium and sodium analogues reacted with alkyl or aralkyl halides in hexane or heptane solvent, it is apparent that the polar halide is absorbed from the solution and reacts with the organometallic compound much more readily than does the 9-monoalkylated fluorene, which escapes into solution largely before it reacts further. The small amount of disubstituted fluorene actually observed in the case of the potassium salt in hexane arises no doubt from a scheme such as suggested above, due to the greater ionic character of the C-K bond.

The electron donor properties of ethers, however, causes some of the salt to be soluble in some ethers, e.g. dioxane, while most or all of the alkali metal compound is dissolved in other cases, e.g. ethers of ethylene glycol and tetrahydrofuran. In solution, because of this association of the ether and the organometallic compound, the ionic character of the metal-carbon

bond is increased, - more so for the more electropositive metals potassium and sodium than for the lithium. Reaction in solution between the salt and the organic halide therefore is expected to, and actually did occur more rapidly. The newly formed 9-monosubstituted compound, which is also in solution, is thus able to set up an equilibrium similar to that shown above, but involving the solvated organometallic compound and that portion of the 9-fluorenyl metal as yet unreacted. The 9-alkyl-9-fluorenyl-potassium (-sodium or -lithium) can then react with a second molecule of the organic halide to give the disubstituted fluorene. Thus there is produced one molecule of unchanged fluorene for every molecule of disubstituted fluorene. In all the experiments reported in this work there has been no case where more disubstituted than unsubstituted product has been isolated, in agreement with the mechanism just outlined. The position of the equilibrium will then depend upon the relative acidities of the fluorene and monosubstituted fluorene and upon the rapidity with which the organic halide reacts with the monometalated fluorene. The assumption that disubstitution is obtained via the obove equilibrium occurring primarily in solution is supported by greater extent of disubstitution actually found in solvents wherein almost all, if not all, the organometal is dissolved. (Compare results in the accompanying Tables).

Since the lithium derivative gave very little disubstitution in any solvent, even in those where it is quite soluble, it is obvious that the extent of ionic character of the

carbon-metal bond is an important factor which determines the degree to which such an equilibrium can be established in competition with the direct reaction of the monometalated compound with the alkyl halide.

e) The Acidity of Fluorene and its C_9-Substituted Derivatives.

Usually alkylation at a carbon atom reduces the acidity while arylation increases the acidity of the remaining hydrogen(s) at the same carbon atom. The greater acidity of 9-phenylfluorene over that of fluorene has been recorded in the literature (4, 5), but no report compares the acidity of 9-alkylated fluorene with that of the parent compound. However, since the disubstituted fluorene derivatives, actually observed in this work, were most likely produced via crossmetalation between metalated fluorene and 9-alkylfluorene, - there was no other source of metal available, especially in the more effective ether solvents where clear solutions of the organometallic compound were obtained, - it may be assumed that the acidity of 9-alkylfluorenes is at least of the same order as, but more likely greater than, that of fluorene itself. Otherwise the 9-alkylated fluorenes could not compete as successfully as they did with the polar bond in the organic halide

for the organometallic compound. No differentiation in the acidity of various C_9 -monoalkylated fluorene derivatives was shown from the results of the reactions of 9-fluorenylpotassium with the halides methyl iodide, ethyl bromide, allyl bromide and benzyl chloride in dioxane since approximately the same extent of disubstitution occurred in each, regardless of the nature of the group. This lack of differentiation might be due, as already mentioned, to the highly reactive and therefore less discriminating potassium-carbon bond.

There exists the possibility that some, if not all of the disubstitution might be due to unreacted metal, occluded in the organometallic compound, which would react with the monosubstituted fluorene during the process of addition of the alkyl halide. A report is found in the literature (55) that describes such a highly dispersed state of potassium metal in a solvent so as to render it indiscernible to the eye when the solution is cooled. The rate of stirring employed in the present experiments, however, certainly would not lead to such an ultra-fine state of division of the metal, hence any substantial quantity of it which remained unreacted should be readily seen in the cases where clear solutions are obtained.

In order to determine if the presence of unreacted metal actually did play a part in producing disubstituted fluorene an experiment was performed in which the reaction between equimolar quantities of fluorene and potassium

metal was allowed to proceed for just 15 minutes, after which some of the potassium metal was still unreacted. To this mixture an equimolar amount of methyl iodide was added and the product separated as usual. A yield of 30 per cent of dimethylfluorene, and 18 per cent of monomethylfluorene was obtained, the remainder being unchanged fluorene. Since the corresponding experiment in which all the metal had apparently reacted to form 9-fluorenyl-potassium gave 35 per cent dimethylfluorene and 30 per cent monomethylfluorene, the conclusion must be made that in those cases where unreacted metal did remain, the metal did cause dialkylation, somewhat more than in those reactions where only 9-fluorenylpotassium was present. But this again requires the assumption that the substituted fluorene must be slightly more acidic than fluorene itself in order to compete so successfully for the metal. However, in those solutions, where complete reaction of metal with fluorene had occurred, all disubstitution must be obtained through crossmetalation as indicated in the aforementioned equilibrium.

The study of the NMR spectra of fluorene, 9-methylfluorene, 9-benzylfluorene and 9-phenylfluorene furnished some more evidence that 9-alkylfluorenes do in fact possess somewhat greater acidity than the parent fluorene. The tendency of the C_9 substituent to become coplanar with the planar fluorene moeity, which is supposed to be the cause of the increased acidity, would assist the tendency of carbon 9 to rehybridization from

sp^3 to sp^2, in agreement with the known capability of fluorene for carbanion formation (5, 52, 53). Several reports concerning nuclear magnetic resonance studies show that the chemical shift observed for the proton signal is related to the electronic environment and hence the acidity of the proton (56, 57).

Table X shows the position of the C_9 proton signal, referred to the proton signal of the chloroform solvent for each of the compounds under investigation. The large shift of 63 cycles per second for the proton signal in 9-phenylfluorene is clearly an indication of the marked acidity actually found for 9-phenylfluorene. (2, 3). Both 9-methylfluorene and 9-benzylfluorene show a shift of only 12 c/s relatively to fluorene but in the same direction as that found for 9-phenylfluorene. This supports the view that the proton on carbon 9 of these monoalkylated fluorenes is also more acidic than the proton in unsubstituted fluorene.

Table X

NMR Signals of the C_9-Proton of Fluorene and C_9-Substituted Derivatives.

Compound	Signal relative to solvent (cycles/sec.)	Shift relative to fluorene (cycles/sec.)
Fluorene	+ 193	0
9-Phenylfluorene	+ 130	- 63
9-Methylfluorene	+ 181	- 12
9-Benzylfluorene	+ 181	- 12

5. The Hydrogen-Deuterium Exchange between Fluorene and Deuterium Oxide in Ether Solvents.

The presence of dideuterated fluorene in a product obtained from the reaction of 9-fluorenylpotassium and an excess of deuterium oxide led to the investigation of the hydrogen-deuterium exchange in fluorene. The spectrum of the product, originally thought to be essentially 9-deuterofluorene, is shown in (Fig. 25). Three bands on the right-hand side of the spectrum, 692, 677 and 667 cm^{-1} can be used to evaluate the relative amounts of fluorene, mono- and dideuterated fluorene in a mixture of these compounds. The absence of any significant absorption at 692 cm^{-1} (Fig. 25) shows that essentially no fluorene is left unchanged. The greater area of the 667 cm^{-1} band, which is now definitely assigned to the $>CD_2$ grouping, compared to the area of the 677 cm^{-1} band, which is due to the $>CHD$ group, shows that actually more dideuterated than monodeuterated fluorene is present. This was confirmed by the NMR analysis, which indicated the absence of unchanged fluorene but the presence of dideuterated material to a considerable extent in this "monodeuterated fluorene". At first it was believed that the difference between these two bands, 667 cm^{-1} and 677 cm^{-1} represented the amount of dideuterated material, since the 667 cm^{-1} band was believed to originate from the C-D bond, whereas the 677 cm^{-1} then stemmed from the remaining C-H bond of the monodeuterated fluorene. The change in assignment of the 667 cm^{-1} band to represent the $>CHD$ group was mainly the result of the

examination of the hydrogen-deuterium exchange and the experiments with 9-fluorenyllithium. The monodeuterated fluorene obtained from the 9-fluorenyllithium showed nearly total absence of the 667 cm^{-1} band (Figs. 2, 24). The NMR analysis of the product obtained from the reaction of equimolar amounts of 9-fluorenyllithium and deuterium oxide in dimethoxyethane showed a signal for the proton at C_9 (Fig. 20a), which is nearly half that found for the protons at C_9 of the parent fluorene (Fig. 20b). The broadening of the signal in Fig. 20a is probably due to spin coupling of the proton with the deuterium atom. Fluorene and dideuterated fluorene were only minor contaminants of this product.

Monodeuterated fluorene made from equimolar amounts of 9-fluorenyllithium and deuterium oxide in hexane as solvent was not contaminated by dideuterated fluorene at all. This is shown in Fig. 2, which shows no absorption at 667 cm^{-1}. All other bands of the spectrum are in full agreement with these interpretations as had been shown in a previous discussion of the present work.

The occurrence of hydrogen-deuterium exchange in fluorene in the presence of the metal deuteroxides formed in the reaction must therefore account for the accompanying dideuteration observed in many of the deuteration experiments, where monodeuteration only should occur. That such exchange does occur was at first shown in two test cases. The first involved the reaction of equimolar amounts of fluorene, deuterium oxide

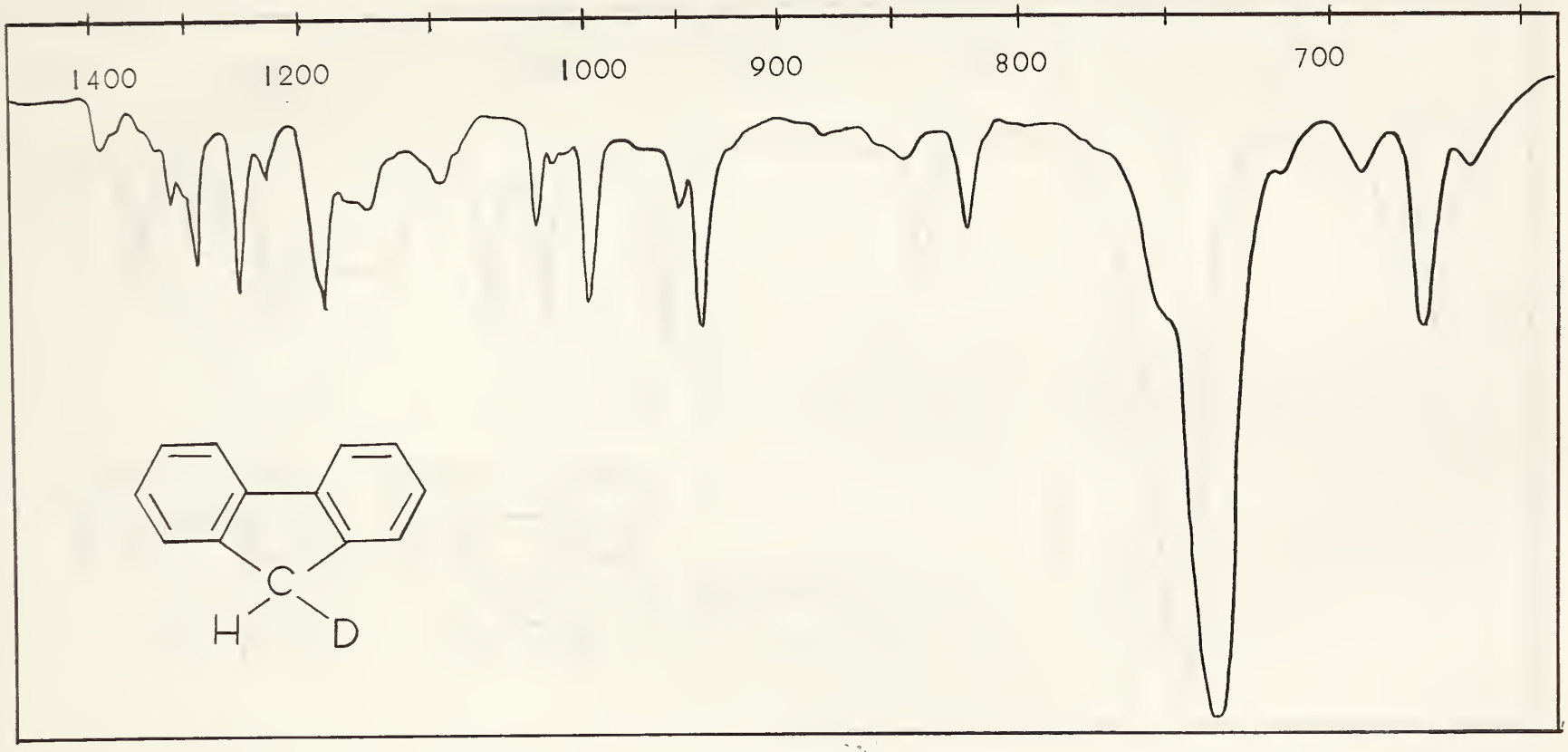


Fig. 24 Partial infrared spectrum of 9-deuterofluorene (contaminated by some fluorene and 9,9-dideuterofluorene) in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

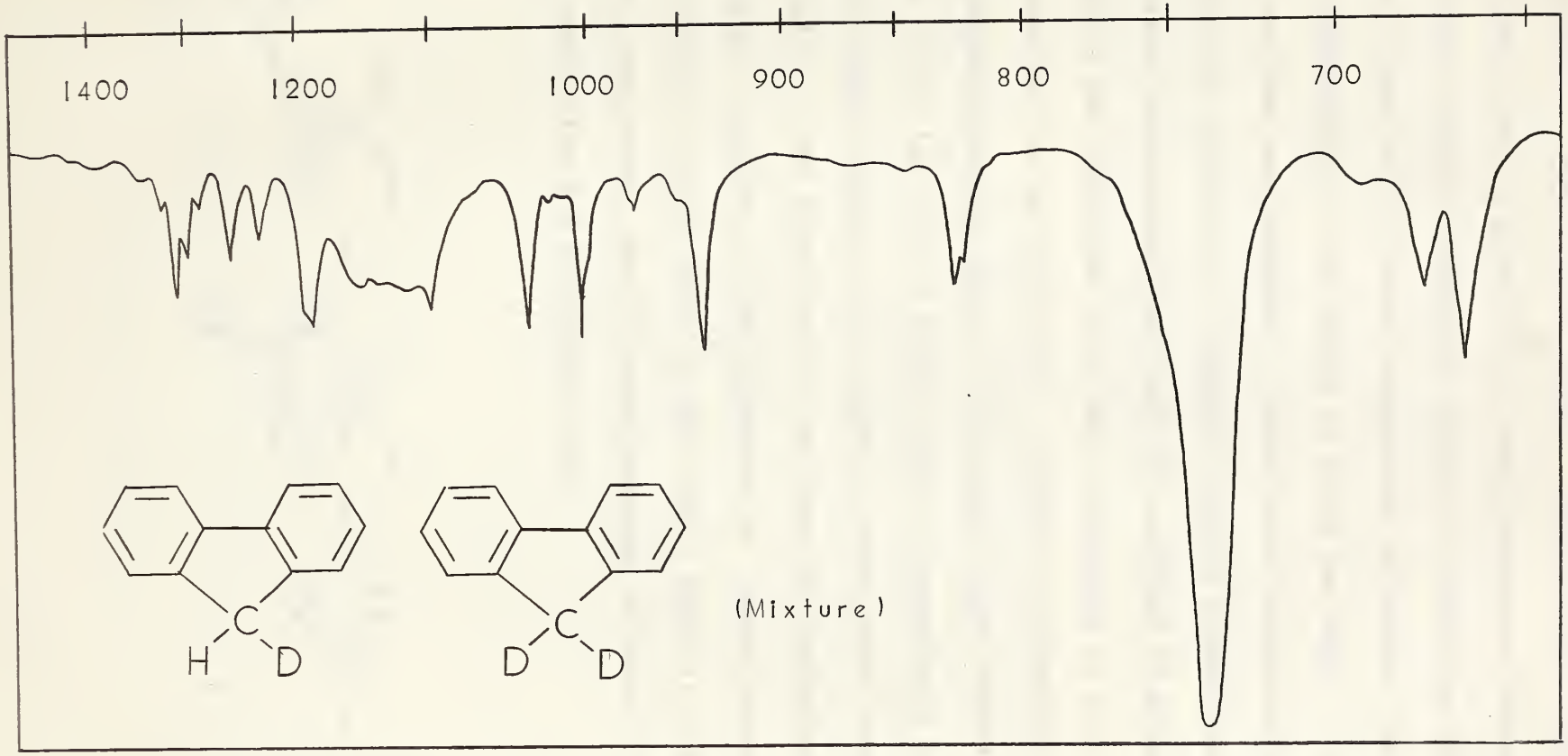
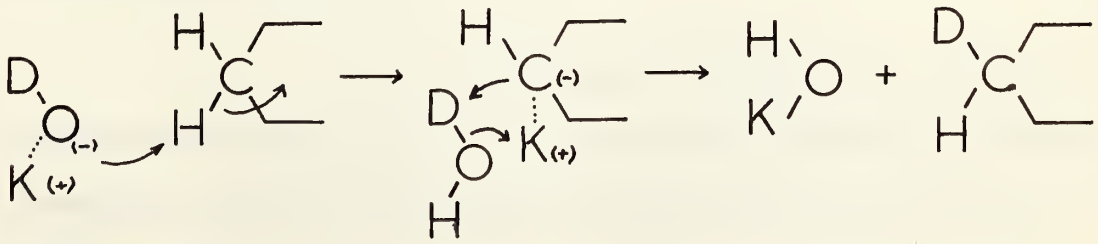


Fig. 25 Partial infrared spectrum of 9-deuterofluorene and 9,9-dideuterofluorene in CS_2 showing the 1450-600 cm^{-1} region (Perkin Elmer 21)

and potassium hydroxide in dioxane solvent kept at room temperature for three hours to give 5-8 per cent deuterated fluorene.
The second, wherein equimolar amounts of potassium deuteroxide and fluorene were kept at room temperature in dioxane for one hour, gave deuteration to the extent of 10-15 per cent. If in the latter case the time was extended to three hours, approximately 40 per cent deuteration occurred. The apparent greater effectiveness of the potassium deuteroxide above that of a mixture of potassium hydroxide and deuterium oxide was interesting to note. It may be rationalized on the basis that a distinct intermediate 9-fluorenylpotassium does not form under these conditions. The anion of the ion pair of K-OD, which is essentially undissociated in the ether solvents, will remove a proton from fluorene, but the proximity of the potassium ion may cause an instantaneous subsequent reaction of the carbanion in "statu nascendi" with the material closest to it at that time, which is the HOD, itself in the same state. The following sequence of steps illustrate how the deuteration may be brought about:



Such instantaneous reaction of the carbanion with the water formed in the first stage of the reaction is reasonable since water is a much stronger acid than is fluorene. The KOH formed via this sequence may react again with the resulting deuterofluorene to remove either the hydrogen or the deuterium atom from the fluorene molecule, but preferentially the hydrogen due to an isotope effect. The removal of deuterium would lead to a reconversion of the deuterofluorene to fluorene and KOD, whereas the removal of hydrogen leaves the deuterofluorene intact.

In the case of fluorene reacting with a mixture of equimolar amounts of KOH and D_2O the postulation on an instantaneous reaction of the 9-fluorenylpotassium with the simultaneously formed molecule of water may be used to explain the observed lower yields of deuterated fluorene obtained from such a mixture as compared to the larger extent of deuteration, which resulted from the reaction of KOD and fluorene. The reaction of KOH and fluorene followed by the reaction with D_2O would also lead to deuterated fluorene. This occurrence, however, competes with the reaction of the intermediate 9-fluorenylpotassium with the water molecule formed at the site of the metalation reaction.

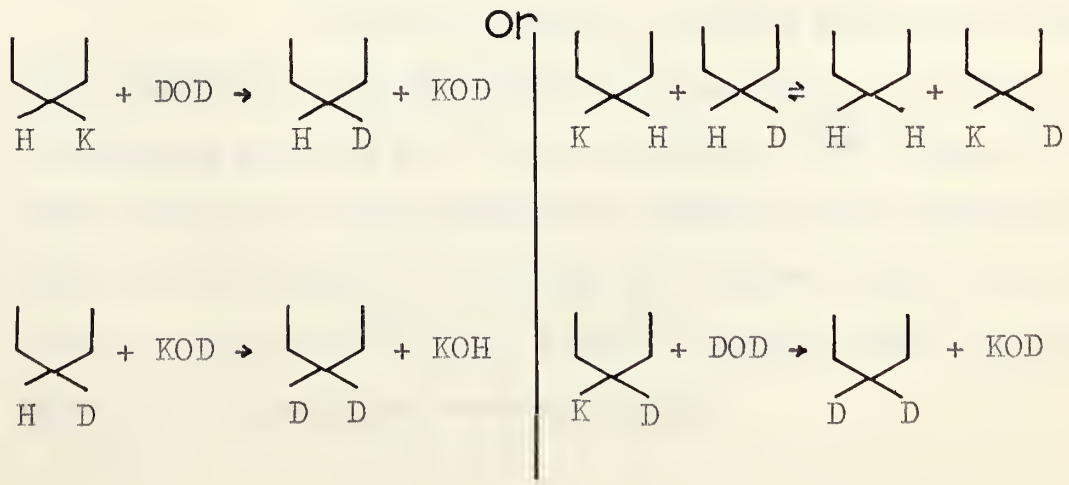
On the other hand one might assume that all deuterated fluorene arises from the action of KOD only. KOD is certainly formed in the mixture of KOH and D_2O due to the equilibrium

$$KOH + DOD \rightleftharpoons KOD + HOD$$

since KOH and D_2O are, no doubt, closely associated in dioxane solution. This is supported by the observation that KOD remained solid in dioxane solvent, while the addition of even one equivalent of D_2O to either KOH or KOD rendered it soluble in dioxane.

With the knowledge of the exact assignment of the bands due to fluorene, mono- and dideuterated fluorene some experiments on the deuteration of fluorene were carried out. For convenience the mixtures, conditions of reactions and results are compiled in Table XI. The yields of mono- and dideuterated fluorene and unchanged fluorene are estimated from the relative magnitudes of the bands at 677 cm^{-1}, 667 cm^{-1} and 692 cm^{-1} mainly, aided by the other peaks on the spectrum as mentioned earlier.

It is clearly seen that 9-fluorenylpotassium, reacting with an equimolar amount of D_2O, produced less unchanged fluorene and more dideuteration in dimethoxyethane than in dioxane. Such deuteration may occur via the sequence shown:



Unchanged fluorene might come from a) incomplete metalation; b) the small amount of water present in the deuterium oxide; c) a combination of 9-fluorenylpotassium with H_2O or DOH produced in the first part of the reaction. The more extensive dideuteration which occurs in the solvent DME agrees with the greater effectiveness of DME as a solvent in the preparation and reaction of 9-fluorenylpotassium, due to the more effective coordination of the ether with KOD, enhancing the latter's basicity.

9-Fluorenyllithium in dimethoxyethane, on the other hand, gave largely C_9 -monodeuteration accompanied by only a small proportion of dideuterated and unchanged fluorene (Fig. 24). But with the solvent hexane rather than DME, dideuteration was practically eliminated and the extent of monodeuteration increased correspondingly. This spectrum has been considered as the purest monodeuterated fluorene obtained throughout these studies and hence is shown in Fig. 2 as the representative of this compound.

KOD and fluorene in dioxane gave more extensive dideuteration than did KOH and fluorene and D_2O, which had been rationalized above as due to the proximity of the reagent. With DME as the solvent such differences appeared to be minimized and nearly the same amount of exchange was observed. This is in full agreement with the better ion solvating power of DME vs. dioxane shown in the metalation reaction already.

Table XI

Mono- and Dideuteration of Fluorene.

Reagents	Solvent and conditions	CH_2 (%)	CHD (%)	CD_2 (%)
K-fluorenyl + D_2O (excess)	dioxane, room temp. 1 hr.	2	38	60
K-fluorenyl + D_2O	dioxane	35	50	15
K-fluorenyl + D_2O	DME	15	45	40
Na-fluorenyl + D_2O	DME	5	45	50
Li-fluorenyl + D_2O	dioxane + trace DME	20	70	10
Li-fluorenyl + D_2O	DME	12	80	8
KOD + fluorene + D_2O	dioxane (all KOD dissolved)	15	45	40
KOD + fluorene + D_2O	DME (all KOD dissolved, red color within 3 min.)	20	50	30
KOH + D_2O + fluorene	dioxane (all KOH dissolved)	90	10	0

Table XI continued

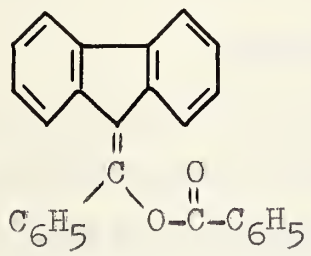
Mono- and Dideuteration of Fluorene.

Reagents	Solvent and conditions	CH_2 (%)	CHD (%)	CD_2 (%)
KOH + D_2O + fluorene	DME (all KOH dissolved)	45	50	5
KOD + fluorene	dioxane (KOD not dissolved)	70	30	0
KOD + fluorene	DME (KOD not dissolved)	45	50	5
LiOD + fluorene	DME (LiOD not dissolved)	100	0	0
LiOD + fluorene + D_2O	DME (LiOD not dissolved)	90	10	0
LiOD + fluorene + 3 D_2O	DME (LiOD not dissolved)	85	15	0
Li-fluorenyl + D_2O	hexane	8	90	2

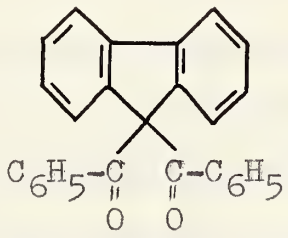
LiOD and fluorene failed to show any exchange when refluxed in dimethoxyethane, but when D_2O was added exchange did occur and increased in magnitude with the amount of D_2O added. This agrees with the interpretation that LiOD under anhydrous conditions is a much weaker base than is either KOD or NaOD and hence will not initiate the first step of the reaction - that of transient formation of the 9-fluorenyllithium. The addition of D_2O yields a solvent which promotes the dissociation or the separation of the ion pair Li-OD to a further degree, which enhances its basicity. Such a leveling effect of solvents has been observed in other cases (58). It might be noteworthy in this connection that the addition of an equimolar amount of D_2O to a mixture of fluorene and KOD in DME solvent was sufficient to dissolve all KOD, whereas LiOD was not dissolved even when three equivalents of D_2O were added.

6. The Reactions of Benzoyl Chloride and Ethyl Benzoate with the Alkali Derivatives of Fluorene.

In view of the finding that the relative amount of mono- and dialkylation at C_9 of fluorene obtained from the reaction of equimolar quantities of alkyl halide and monometalated fluorene depended upon the metal and solvent employed, a study was undertaken of the reaction of benzoyl chloride with some of the alkali metal salts of fluorene in ether and hydrocarbon solvents. Any disubstitution occurring during the benzoylation of the alkali metal derivatives of fluorene may give rise to two products, the enol ester (C) and the β-diketone (D).



C



D

As already mentioned in the literature survey, both compounds have been observed in previous work. Schlenk and Bergmann (32) unknowingly obtained a small amount of 9,9-dibenzoylfluorene from the reaction of 9-fluorenyllithium and

benzoyl chloride in benzene solution. Kliegl, Weng and Wiest (34) isolated 9,1'-benzoyloxybenzylidenefluorene, when they treated 9-fluorenylsodium with benzoyl chloride in ether solvent.

No synthesis has been recorded in the literature for the preparation of pure 9,9-dibenzoylfluorene in reasonable yields.

a) The Reaction of Benzoyl Chloride with 9-Fluorenyllithium, -Sodium or-Potassium.

When 9-fluorenylpotassium was treated at room temperature with benzoyl chloride in either dioxane or diethyl ether, wherein the salt is only partly soluble, the major product consisted of 9-1'-benzoyloxybenylidenefluorene.

The expected 9-benzoylfluorene was obtained only as a minor product and could be removed quite readily, along with much unreacted fluorene, by boiling the solid reaction product with ethyl alcohol, in which the enol ester is insoluble. The same result was obtained when the solid 9-fluorenylpotassium, freed from dioxane solvent, was suspended in pentane and treated with benzoyl chloride. Similar results were obtained when 9-fluorenylpotassium, completely dissolved in dimethoxyethane, or 9-fluorenylsodium dissolved in dimethoxyethane or diethoxyethane, was allowed to react with benzoyl chloride.

On the other hand, the reaction of 9-fluorenyllithium and benzoyl chloride gave results quite different from those obtained with the sodium or potassium analogues. Under the heterogeneous conditions obtained in the suspension of the lithium salt in pentane, 9,9-dibenzoylfluorene was produced in 28 per cent yield, uncontaminated by the enol ester (C). The unreacted fluorene, along with a small amount of monobenzoylfluorene, was easily removed by extraction from the insoluble β-diketone (D) with hot ethanol. However, equimolar amounts of 9-fluorenyllithium and the acid halide in diethoxyethane or dimethoxyethane yielded a mixture of 9,9-dibenzoylfluorene and 9-1'-benzoyloxybenzylidenefluorene. Efforts to separate this mixture were unsuccessful. The infrared spectra, obtained for both C and D , clearly showed the presence of this mixture. (Figs. 26 - 28).

The infrared spectrum of the 9-1'-benzoyloxybenzylidenefluorene (Fig. 26) in carbon disulphide showed a strong band at 1738 cm^{-1}, typical of a conjugated ester carbonyl group, and a band of medium strength at 1650 cm^{-1} due to the enol double bond. (39). The enol ester showed no absorption at 1688 cm^{-1}. The spectrum of the 9,9-dibenzoylfluorene (Fig. 27) exhibited a strong doublet at 1688 cm^{-1} and 1660 cm^{-1}, but no absorption at 1738 cm^{-1}. The presence of one isomer as an impurity in the other was thus easily detected by the bands at 1738 cm^{-1} and 1688 cm^{-1}.

A further distinct difference occurred in the region of the aromatic C-H out-of-plane bending frequencies. The β-diketone showed one sharp band of medium intensity at 762 cm^{-1}, whereas the enol ester gave two sharp bands, one at 762 cm^{-1}, the other at 775 cm^{-1}.

The spectrum of 9-benzoylfluorene, which is not shown here, exhibited a doublet at 1670 cm^{-1} and 1688 cm^{-1}, though not as well resolved as that found for the diketone. In addition, a strong band at 1273 cm^{-1} and a weak band at 1723 cm^{-1} occurred in the spectrum of the monobenzoylfluorene but not in that of the diketone. The 9-benzoylfluorene is considered to exist in the more stable keto form (59). The double carbonyl band of the keto form of 9-benzoylfluorene is not unusual since this phenomenon has been observed in a number of compounds containing only one carbonyl group (60).

b) The Reaction of Ethyl Benzoate with 9-Fluorenyllithium, -Sodium and -Potassium.

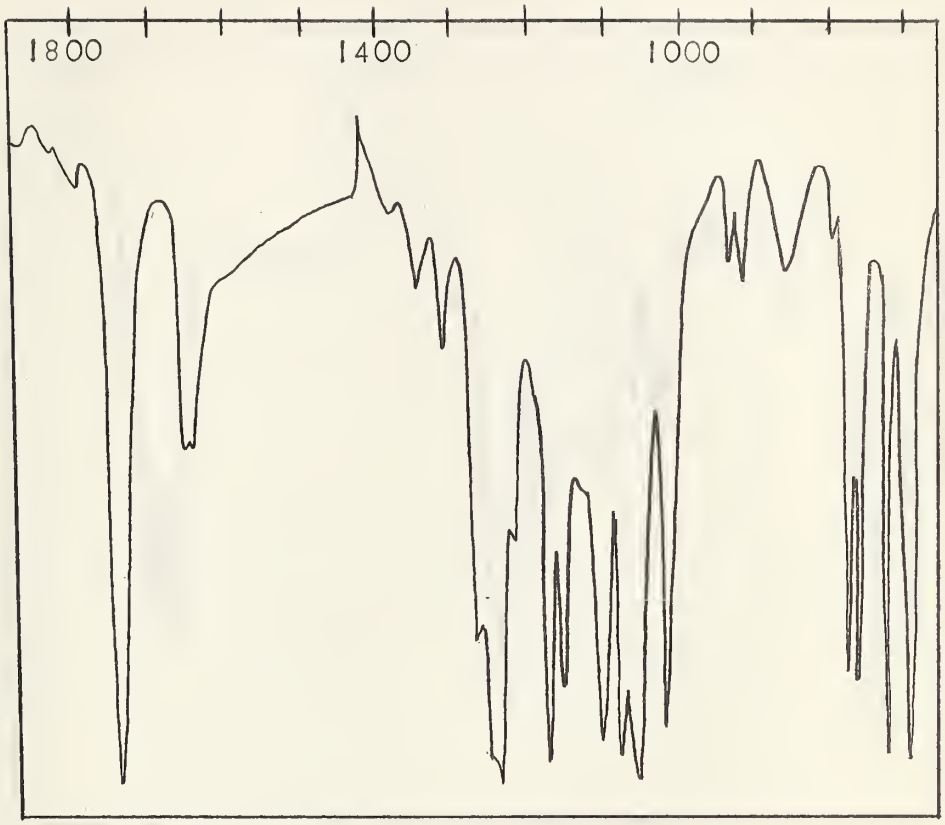
The reaction of 9-fluorenylpotassium, either in dioxane or pentane, with ethyl benzoate gave a 40 per cent yield of 9-benzoylfluorene. This is a considerably better yield of monobenzoylated fluorene than that of 28 per cent obtained by Wislicenus and Fehrle (37) from the reaction of fluorene, potassium and ethyl benzoate mixed in the ratio 1 : 1 : 1. The reaction of 9-fluorenyllithium, either partly dissolved in dimethoxyethane or as an insoluble suspension in pentane, when subsequently

treated with ethyl benzoate gave 40 - 45 per cent of 9-benzoylfluorene. In all cases much fluorene was isolated, but no evidence was found for the formation of the enol ester C, or the diketone D.

c) The Reaction of 9-Benzoyl-9-Fluorenyllithium -Sodium, or -Potassium with Benzoyl Chloride or Ethyl Benzoate.

The compound 9-benzoylfluorene was converted readily to the lithium, sodium or potassium salt and then brought into reaction with benzoyl chloride or ethyl benzoate. In the ether solvents, dimethoxyethane or diethoxyethane, 9-benzoyl-9-fluorenyllithium and benzoyl chloride produced 55 - 60 per cent of an inseparable mixture of enol ester and diketone. But when pentane was the solvent, a 54 per cent yield of diketone was obtained, uncontaminated by enol ester. The sodium salt in dimethoxyethane or diethoxyethane, and the potassium salt in dimethoxyethane gave a 50 - 60 per cent yield of the enol ester uncontaminated by the diketone.

The potassium or sodium salt of 9-benzoylfluorene in dimethoxyethane, reacting with ethyl benzoate, produced only unchanged 9-benzoylfluorene.



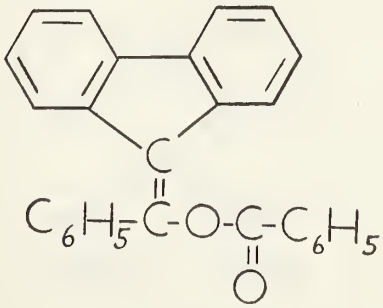
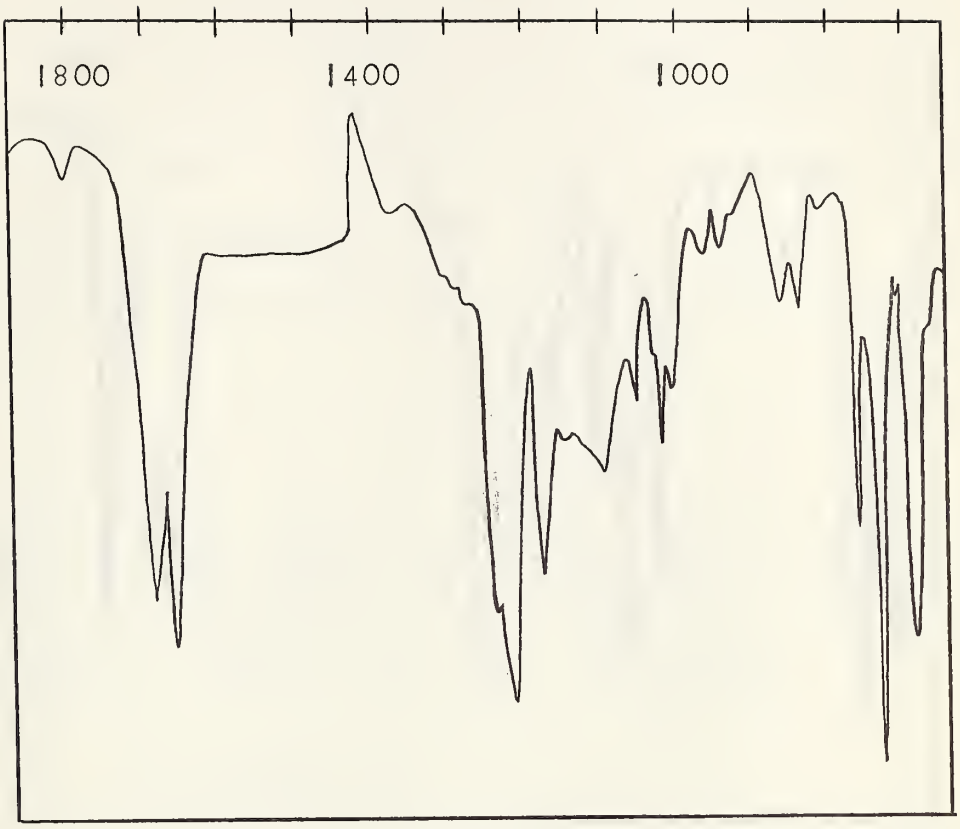


Fig. 26

Partial Infrared spectrum of

9-1'-benzoyloxybenzylidenefluorene in CS_2

showing the 1800-700 cm^{-1} region (Perkin Elmer 221)



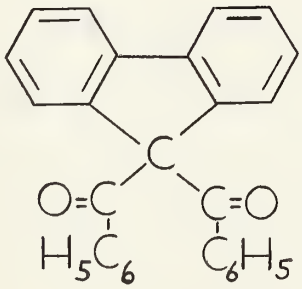
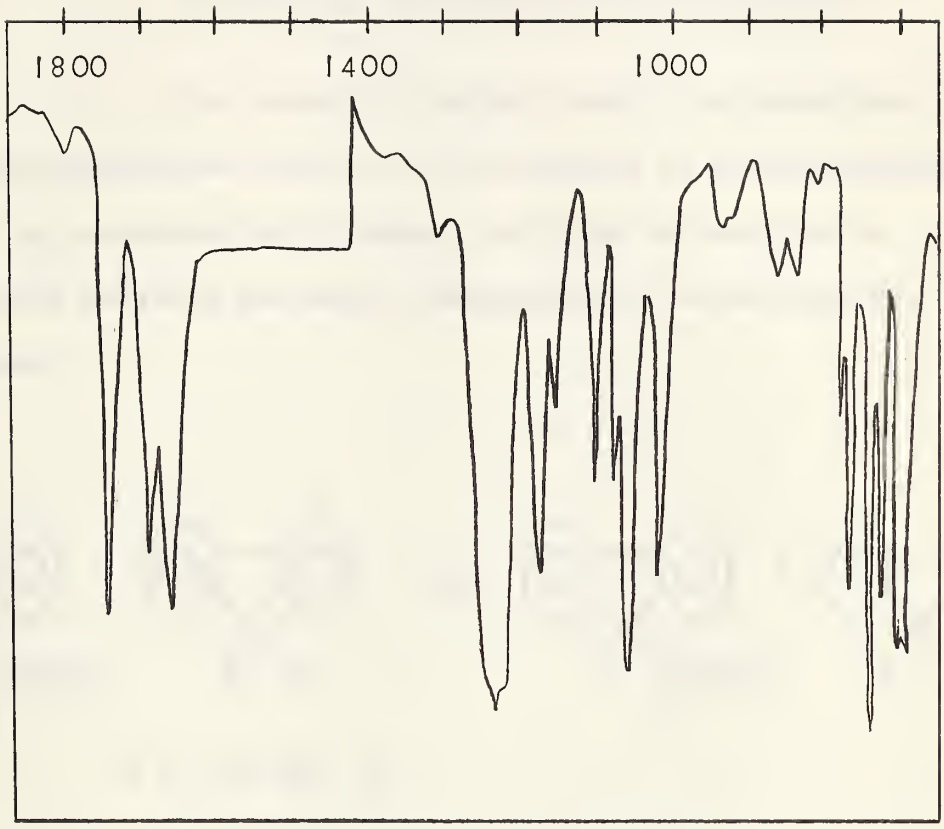


Fig. 27

Partial infrared spectrum of

9,9-dibenzoylfluorene in CS_2

showing the 1800-700 cm^{-1} region (Perkin Elmer 221)



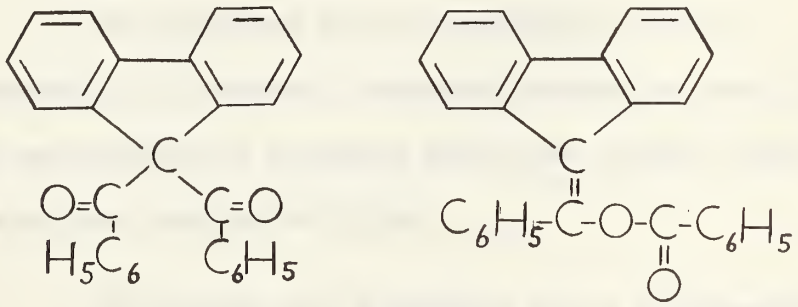
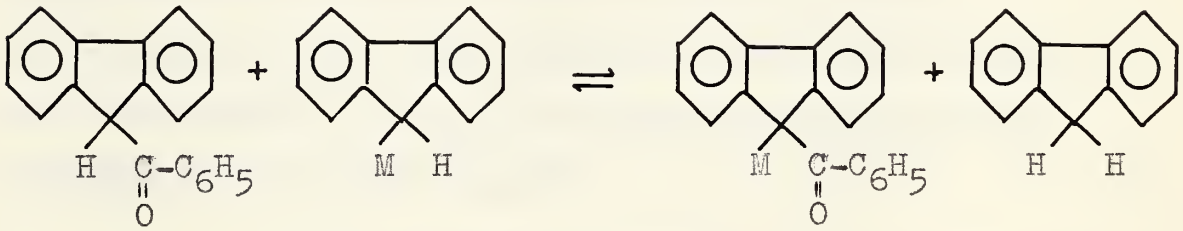


Fig. 28

Partial infrared spectrum of 9,9-dibenzoylfluorene and 9-1'-benzoyloxybenzylidenefluorene in CS_2 showing the 1800-700 cm^{-1} region (Perkin Elmer 221)

d) The Influence of the Metallic Cation and Solvent on the Benzoylation of Fluorene.

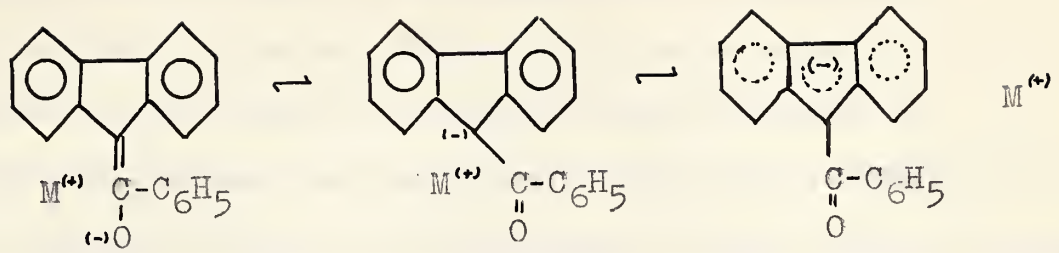
The results obtained clearly indicate that the following equilibrium occurs in the reaction of 9-fluorenyllithium, -sodium or -potassium with benzoyl chloride in ether or in hydrocarbon solvents and under homogeneous or heterogeneous conditions:



M = Li, Na, K .

The enhanced acidic character of the remaining hydrogen at C_9 causes 9-benzoylfluorene to react with the remaining monometalated fluorene much more readily than the latter does with the benzoyl chloride.

The sodium and potassium salts of 9-benzoylfluorene will be largely, if not completely, ionic and stabilized by contributing structures E, F and G.



E F G

The highly ionic C-M bond will favor the more stable enolate ion where the charge resides on the more electronegative oxygen atom. Hence the enolate ion, E, rather than the carbanion, F, will be the species reacting with the remainder of the benzoyl chloride.

The carbon-metal bond of 9-benzoyl-9-fluorenyl-lithium, on the other hand, is essentially covalent and remains so when the organometallic compound is suspended in pentane. Reaction with benzoyl chloride then occurs apparently exclusively at the polar carbon-metal bond to form 9,9-dibenzoylfluorene. However, in ether solvents, particularly dimethoxyethane and diethoxyethane, some association occurs between the metal and the unshared electron pairs of the oxygen atoms, thus enhancing the ionic character of the carbon-lithium bond. This ionic character will then permit some contribution of the enolate form, E. Benzoyl chloride then will react competitively with both enolate ion, E, and carbanion, F. The extent of the enolate form must

depend upon the degree of electropositivity of the metal, as determined by the association of the latter with the solvent, rather than be due simply to slow attainment of equilibrium between the ions E and F. This view is supported by the fact that the same relative amounts of enol ester and diketone were obtained whether 9-benzoyl-9-fluorenyllithium was allowed to remain in the ether solvent a very short time or as long as 10 hours before reaction with benzoyl chloride occurred.

The above viewpoint explains why 9-benzoylfluorene, converted to the alkali metal salt and then allowed to react with benzoyl chloride, produced only the enol ester, C, if the metal was sodium or potassium, but only the diketone, D, in pentane, or a mixture of C and D in ether solvents when the metal was lithium.

The formation of only 9-benzoylfluorene along with unchanged fluorene from the reaction of ethyl benzoate and 9-fluorenyllithium, -sodium or -potassium in ether or hydrocarbon solvents is no doubt due to the lower nucleophilic character of the enolate ion, E, or the carbanion, F, as compared with that of the ethoxide ion. The ethoxide ion, which must be formed if either the enolate ion or the carbanion reacts with ethyl benzoate, readily reacts with the enol ester or β-diketone to form the resonance stabilized monobenzoylfluorenyl anion (E F G). Such a decomposition of an enol ester or diketone by a strong base has been shown previously (35, 37).

The failure of Grignard reagents to form the expected tertiary alcohol from 9-methyl-9-benzoylfluorene also demonstrated the labile nature of 9-benzoylfluorene under basic conditions (61). A similar explanation has been offered for the failure of metalated diphenylmethane to react with more than one equivalent of ester (62).

EXPERIMENTAL SECTION

1. The Preparation of C_9-Substituted Derivatives of Fluorene.

Fluorene.

The fluorene used in this work was Eastman Kodak 98 % practical grade. For the infrared work it was recrystallized from alcohol. All reactions involving the preparation of organometallic compounds were protected by an atmosphere of purified dry nitrogen.

9-Fluorenylpotassium.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were heated in refluxing pure dioxane protected by an atmosphere of purified dry nitrogen. In 3 hours all the potassium was consumed. The reaction mixture was cooled to room temperature and the reddish-brown precipitate isolated by filtration under suction and washed with dry hexane to remove unreacted fluorene. Isolation of the monopotassium compound was best carried out in a dry box containing an atmosphere of nitrogen. Samples for analysis were prepared by freeing the 9-fluorenylpotassium from adhering solvent with a stream of nitrogen drawn through the solid product by suction. Analysis was carried out by first treating a weighed portion of the solid with water then titrating the basic solution with standard acid.

9-Fluorenyllithium.

Fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole), cut into small pieces of about 1 mm^3 were refluxed in pure dry 1,2-diethoxyethane. After 5 hours of reaction all lithium appeared to have reacted. The reaction mixture was cooled to room temperature and poured into an excess of dry hexane (dried over potassium wire). The solid, orange-red 9-fluorenyllithium was washed several times with dry hexane. It can be stored under this solvent in a closed bottle for at least two days. Solid 9-fluorenyllithium can be conveniently transferred into any other inert solvent for subsequent reactions.

9-Deuterofluorene.

9-Fluorenyllithium, prepared from fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole) in refluxing 1,2-diethoxyethane, and subsequently freed from the ether solvent by several hexane washings, was suspended in 100 ml of dry hexane. D_2O (1.0 g, 0.05 mole) was added. The reaction occurred readily, but stirring was continued for 1 hour at room temperature. The reaction mixture was then poured into a separatory funnel and washed with water. The hexane layer was dried over calcium chloride, followed by evaporation of the solvent. The product was recrystallized from ethyl alcohol. The infrared spectrum is shown in Fig. 2. The product consisted of 90 % C_9-monodeuterated fluorene, contaminated by about 8 % unreacted fluorene and 2 % dideuterated fluorene.

9,9-Dideuterofluorene.

A mixture of 0.01 mole (1.66 g) of fluorene and 0.02 mole (0.78 g) of potassium metal was heated for 3.5 hours in 5 ml of refluxing dioxane till all the potassium had been consumed. The addition of 1.5 ml of D_2O and isolation of the product as before gave 1.56 g of dideuterated fluorene. The infrared spectrum is shown in Fig. 3. NMR analysis showed complete absence of absorption at the position attributable to the $>CH_2$ group, indicating complete dideuteration.

9-Methylfluorene.

This compound was prepared by the following modification of Greenhow's procedure (19). Fluorene (18 g) and finely powdered sodamide (3.9 g) were heated in a nitrogen atmosphere for 5 hours at 180° C in 50 ml of decahydronaphthalene (dried with sodium and distilled). When the reaction mixture had cooled to room temperature, the solvent was decanted and the remaining black amorphous solid which adhered to the lower portion of the flask was washed several times with sodium dried hexane. Methyl iodide (12 ml) in 50 ml of hexane was then added and the magnetically stirred mixture refluxed for 12 hours under nitrogen. After the cautious addition of water to dissolve the potassium iodide, the hexane layer was separated, dried, and the solvent removed. The yellow oil obtained, dissolved in pentane and cooled in a refrigerator, deposited unchanged fluorene. Further purification was accomplished by chromatography of the pentane mother

liquor on a 50 cm column of dry, activated alumina (80 - 200 mesh). The first fraction, obtained by elution with hexane, gave 9-methylfluorene, m.p. 43 - 44° C. Further purification by repeated chromatography altered the infrared spectrum slightly and changed the melting point of the compound to 45 - 46° C, lit. 45 - 47° C (19). (Compare the melting point of 58° reported by Wieland (63). The infrared spectrum is shown in Fig. 4.

9,9-Dimethylfluorene.

A solution of 16.6 g of fluorene in 80 ml of dioxane, containing 7.8 g of potassium, was boiled for 5 hours under an atmosphere of nitrogen. All the potassium was consumed in this time. The slow addition of 20 ml of methyl iodide, to the cooled mixture, produced a vigorous but controllable reaction. Stirring was continued for 1 hour whereupon both ether and water were added to the reaction flask. Several extractions of the ether solution with water removed the dioxane. The dried ($CaCl_2$) solution was freed from ether and gave a yellow oil which could not be purified adequately by fractional distillation. However, chromatography with alumina of an hexane solution of this oil separated the unchanged fluorene and monomethyl compound from dimethylfluorene. The first fraction gave the 9,9-dimethylfluorene, m.p. 88 - 89° C, but when it was crystallized from methanol it melted at 95 - 96° C. It is interesting that recrystallization from pentane of the 95 - 96° C. melting compound gave a lower and less definite melting point, found in one case to be 78 - 83° C,

which after a second crystallization from pentane gave 81 - 87°C. The infrared spectrum is shown in Fig. 7.

9-Deutero-9-methylfluorene.

Potassium metal (0.39 g, 0.01 g-atom) and 9-methylfluorene (1.9 g, 0.01 mole) were refluxed in dioxane (5ml) for 1 hour. After this time all the metal had reacted and deuterium oxide (1 ml, excess) was added. After a stirring period of 1 hour the reaction mixture was poured into a separatory funnel containing ether and water. The ether layer was separated and after evaporation of the solvent left a yellow oil, which was purified by chromatography. The infrared spectrum of the purified material, m.p.45.5°C, is shown in Fig.6.

9-Ethylfluorene.

This compound was prepared by a modification of Greenhow's method (19). Fluorene (36 g) and sodamide (7.8 g) were refluxed in decahydronaphthalene (80 ml). After a heating period of 5 hours the reaction mixture was cooled to room temperature, followed by decantation of the decalin, which was subsequently replaced by hexane (100 ml). Ethyl iodide (40 ml, excess) was added and the mixture refluxed for 12 hours. Addition of water removed the inorganic products. The hexane layer was dried over calcium chloride and the solvent then evaporated, whereupon 34.9 g of a yellow oil was left. Vacuum distillation gave 26.0 g of a light yellow oil, b.p. 130° - 132° C at 3 mm Hg, which was 9-ethyl-

fluorene, contaminated by some fluorene. Further purification was achieved by elution chromatography.

9,9-Diethylfluorene.

Fluorene (33.2 g, 0.2 mole), dissolved in pure dry dioxane (180 ml), was refluxed with potassium metal (15.6 g, 0.4 mole) for 5 hours under an atmosphere of nitrogen. Apparently all potassium was consumed after this time and a heavy brown precipitate in a reddish-brown solution was formed. The reaction mixture was cooled to room temperature and ethyl bromide (50 ml, slight excess) added slowly in order to keep the exothermic reaction under control. Stirring was continued over night. The product was isolated by pouring the dioxane solution into a separatory funnel containing ether and water. The ether layer was dried with $CaCl_2$. Evaporation of the ether left a yellow oil (38 g).

Fractional distillation under vacuum yielded 3.1 g of a material boiling at 120° - 122° /3 mm, which was identified as being chiefly fluorene. The main fraction, 29.6 g, (66.7 %) boiling at 131° - 135° /3 mm, was largely diethylfluorene. A brown resin-like residue remained in the flask. Both fractions were contaminated by some 9-ethylfluorene. Further purification was accomplished by elution chromatography using absorption alumina as the stationary phase and pentane as the eluent.

9-Benzylfluorene.

The 9-fluorenylsodium was prepared from 18.3 g of fluorene and 3.9 g of sodium amide heated in decahydronaphthalene for 4 hours at 180° under a nitrogen atmosphere (19). The black solid, deposited in the flask, was washed with hexane as in the preparation of 9-methylfluorene and treated with a solution of 40 ml of benzyl chloride in 40 ml of hexane. This mixture was refluxed for 20 hours. The hexane solution was then diluted with ether and added to water to remove the sodium chloride. Evaporation of the ether-hexane solvent gave a yellow amorphous product which after solution in alcohol deposited 12.5 g of crystalline 9-benzylfluorene melting sharply at 134°. Further purification by chromatography on activated alumina raised the melting point to 136°. Recrystallization from alcohol did not raise the melting point. The infrared spectrum is shown in Fig. 10.

9,9-dibenzylfluorene.

(a) From fluorene. To the dioxane (180 ml), containing the product made from 16.6 g of fluorene and 7.8 g of potassium, was added benzyl chloride (21 ml). The product of this reaction, only slightly soluble in ether , was isolated quite simply by the addition of water and ether to the dioxane solution whereupon the solid which formed could then be removed by filtration. The 9,9-dibenzylfluorene weighed 11.2 g and melted at 146° (from alcohol).

(b) From 9-benzylfluorene. A mixture of 2.6 g of 9-benzylfluorene and 0.39 g of potassium metal (equimolar portions) in 12 ml of dioxane was heated till solution of the metal was complete. 40 minutes of refluxing with 1.2 ml of benzyl chloride gave a solid, isolated as above, with properties and melting point identical with those of 9,9-dibenzylfluorene. The infrared spectrum is shown in Fig. 12.

9-Deutero-9-benzylfluorene.

Dioxane (15 ml) containing 2.56 g of 9-benzylfluorene and 0.39 g of potassium was boiled for 40 minutes, cooled to room temperature, and treated with 0.8 ml (excess) of D_2O. The red precipitate disappeared and the product, isolated as usual by employing ether and water, and crystallized from alcohol, melted at 131° C (yield o.5 g). Chromatography raised the melting point to 134° C, which crystallization from alcohol did not change. The infrared spectrum is shown in Fig. 11.

9-Benzylidenefluorene.

The procedure was a modified version of that employed by Thiele and Henle (7). The use of potassium ethylate gave the product in 3 days as compared with 14 days reported for Thiele and Henle's method.

To a solution of 2.5 g of potassium in 125 ml of dry ethyl alcohol was added 5 g of fluorene. Freshly distilled benzaldehyde (4.5 g) in 10 ml of alcohol was added and the

reaction mixture kept at 45° C for 3 days. The 9-benzylidene-fluorene (3.6 g), deposited from the solution, was crystallized once from alcohol, m.p. 74° - 75° C, lit. 76° C (7).
The infrared spectrum is shown in Fig. 15.

9-Allylfluorene.

This compound was prepared by a modification of Greenhow's method (19). Sodamide (3.9 g) and fluorene (18 g) were heated in refluxing decalin (40 ml) for 4 hours (nitrogen atmosphere). The decalin was then replaced by pentane (50 ml) and the 9-fluorenylsodium treated with 50 ml of allyl bromide (excess). After 8 hours reflux, the product was isolated by removing the sodium chloride with water, then eliminating the solvent as well as the excess allyl bromide. Vacuum distillation gave 11.5 g of a light-yellow liquid, boiling at 132° - 137° C /3 mm. Elution chromatography as described for the methylated fluorene gave a sample suitable for infrared analysis.
The infrared spectrum is shown in Fig. 13.

9,9-Diallylfluorene.

Fluorene (8.3 g) and potassium metal (3.9 g) were boiled for 4 hours in 100 ml of dioxane (N_2). When the reaction mixture was cooled to room temperature and treated with 8.65 ml of allyl bromide, added dropwise, an exothermic reaction occurred with simultaneous disappearance of the reddish-brown precipitate. After an additional period of stirring for 5 hours

the product was isolated as usual by the addition of ether and water. The crude oil (12.1 g) obtained from the ether layer was fractionally distilled under vacuum to yield 7.9 g of a light yellow oil, b.p. 144° C /3mm, which was submitted to chromatography for additional purification. The infrared spectrum is shown in Fig. 14.

Fluorenone.

The fluorenone used for the infrared spectrum was Eastman Kodak whitelabeled material. The infrared spectrum is shown in Fig. 16.

2. The Infrared Spectra.

The infrared spectra of Figs. 1 - 20, 24 and 25 were obtained with a Perkin Elmer model 21 double-beam spectrophotometer, equipped with a sodium chloride prism. The spectra of Figs. 21, 22, 23, 26, 27 and 28 were obtained with a Perkin Elmer model 221.

Solutions in carbon tetrachloride and carbon disulphide , containing 20 mg solute per ml of solvent, were measured in sodium chloride cells of 0.5 mm thickness.

3. Preparation and Reactions of Alkali Metal Derivatives of Fluorene.

Reagents and general conditions.

Eastman Kodak 98 % practical grade fluorene, used without further purification, was found to be quite satisfactory for this work.

Special attention was paid to the solvents. They were generally commercially available reagent grade materials but were further purified by distillation from potassium metal. Only a technical grade of 1,2-diethoxyethane was available. This was treated carefully with potassium , over which the liquid stood for 24 hours. Distillation from the metal gave glycol ether of good quality. After purification all solvents were stored over potassium or sodium wire until required, in order to ensure anhydrous conditions in the metalation experiments. All preparations involving organometallic compounds were carried out under a protective atmosphere of nitrogen. Vigorous stirring was applied in all reactions. In experiments conducted below the melting point of the metal, the metal was cut into very small pieces, about 1 mm^3, before addition to the reaction mixture.

Procedure.

The following is the general procedure which was developed and used without significant changes in all experiments. Details with respect to quantities of reagents and solvents will

be given under the description of the individual experiments in the next section of this thesis.

The alkali metal salt of fluorene, prepared from the reaction of alkali metals and fluorene in the appropriate solvent, was either left dissolved or suspended in the solvent, which had been used for its preparation, or was isolated by pouring the reaction mixture into about five times its volume of dry pentane or hexane. The supernatent liquid was decanted after the metalorganic compound had settled. The precipitate was washed several times and finally left suspended in 100 ml of the hydrocarbon solvent for the subsequent reaction with the alkyl- or aralkyl halide. The reagents, methyl iodide, ethyl bromide, allyl bromide, benzyl chloride or D_2O, usually diluted with the same solvent as was used for the reaction medium in a particular experiment, were added to the organometallic compound slowly in order to avoid uncontrollable reaction. Although the reaction occurred quite readily, especially in ether solvents, a period of stirring of at least one hour at room temperature was allowed in all cases in order to ensure complete reaction of the metal salt with the organic halide. The mixture was then poured into a separatory funnel containing ether and water, slightly acidified with hydrochloric acid. The ether layer was separated and then dried over calcium chloride. The evaporation of the ether solvent left a yellow oily product when the reagents were methyl iodide, ethyl bromide or allyl bromide. Unreacted fluorene

precipitated slowly from these oils. A small portion (usually about 1 gram or less) of the product was separated by chromatography, using an 80 - 200 mesh alumina column, measuring 60 x 1 cm. Hexane or pentane were used as eluting solvents. The fractions emerging from the column were collected on open watchglasses which allowed the solvent to evaporate rapidly. Identification and estimation of the relative amounts of the materials in each fraction (about 100 mg) was made by melting points and/or infrared spectroscopy, using the absorption bands reported in Table II.

It should be noted here that only pure monomethylfluorene (m.p. 43° - 44°) crystallizes readily, since contaminants cause an oily appearance of the product. In all cases the disubstituted compound emerged first from the column, followed by the monosubstituted derivative. Fluorene was the last fraction. When pure fluorene started emerging the elution process was discontinued, since it was found that at this stage only unchanged fluorene was left on the column, which was eluted very slowly by the pentane or hexane solvent. Actually 95 % of the unreacted fluorene could be recovered, when benzene was used as the solvent. The very first fraction sometimes contained solvent impurities, which were taken into account in regard to the sample size. The detailed results are reported under each individual experiment.

Since disubstitution accompanied the normal reaction in most experiments the resulting figures for the amount of mono- and disubstituted material, isolated from the column, were also converted into the amount of fluorene necessary to produce those. The conversion factor in case of dimethylfluorene is 0.855 $\left(\frac{\text{molecular weight of fluorene}}{\text{molecular weight of dimethylfluorene}} = \frac{166}{194}\right)$

The corresponding factors for the other compounds are:

9-methylfluorene	:	0.92
9-ethylfluorene	:	0.85
9,9-diethylfluorene	:	0.75
9-allylfluorene	:	0.81
9,9-diallylfluorene	:	0.67
9,9-dibenzylfluorene	:	0.48

The extent of metalation is then obtained by adding twice the percentage for disubstitution to the percentage of monosubstitution.

The products of the reaction of alkali metal derivatives of fluorene and benzyl chloride could not be resolved on the chromatographic column, due to the low solubility of dibenzylfluorene and to the very close solubilities of fluorene and monobenzylfluorene. 9,9-Dibenzylfluorene was removed from 9-benzylfluorene and unreacted fluorene by means of cold ethyl

alcohol or petroleum ether, in which it is largely insoluble. The yields of the latter two substances could not be determined.

9-Fluorenylpotassium in dioxane.

a) Methylation.

Fluorene (16.6 g, 0.1 mole) and potassium metal (3.9 g, 0.1 mole) were reacted in 100 ml of refluxing dioxane. A reddish brown solution was formed soon after the reaction was started. Brown 9-fluorenylpotassium precipitated as the reaction proceeded. After 4 hours all metal had reacted and methyl iodide (14.2 g) was added to the organometallic compound, whereupon the reaction occurred readily.

A sample of 583 mg of the product, separated on the chromatographic column, consisted of about 150 mg of 9,9-dimethylfluorene, 250 mg of 9-methylfluorene and 183 mg of fluorene, indicating the conversion of 24 % of the original fluorene into its disubstituted derivative and 43 % into the monosubstituted derivative. Hence the extent of metalation was about 91 %. When this experiment was repeated a sample of 864 mg was resolved into 222 mg of 9,9-dimethylfluorene, 348 mg of 9-methylfluorene and 294 mg of fluorene indicating the conversion of 24 % of the original fluorene into its disubstituted derivative and 40 % into the monosubstituted derivative. The extent of metalation was 88 %.

b) Benzylation.

9-Fluorenylpotassium, prepared from fluorene (16.6 g, 0.1 mole) and potassium metal (3.9 g, 0.1 mole) in refluxing dioxane, was reacted with benzyl chloride (12.7 g, 0.1 mole). The product was isolated by means of ether solvent. A yellow solid (22 g) was obtained, which by means of cold petroleum ether was separated into a yellow solution and an insoluble white solid (8.1 g). The latter was identified as 9,9-dibenzylfluorene. Evaporation of the petroleum ether and a tedious recrystallization procedure from alcohol permitted the separation of 2 g of 9-benzylfluorene, contaminated by fluorene.

The isolation of 8.1 grams of 9,9-dibenzylfluorene indicated the conversion of 23 % of the original fluorene into disubstituted derivative.

c) Dimethylation.

Fluorene (8.3 g, 0.05 mole) and potassium metal (3.9 g, 0.1 mole) were allowed to react in refluxing dioxane (80 ml) under vigorous stirring. After 8 hours all of the potassium had apparently reacted, yielding a dark reddish-brown compound, partly in solution. To this reaction mixture methyl iodide (14.2 g, 0.1 mole) was added at room temperature, followed by a one-hour period of stirring. The usual isolation procedure yielded a yellow oil, which slowly deposited fluorene.

A sample of 1000 mg was separated on the chromatographic column into 530 mg of 9,9-dimethylfluorene, 150 mg of 9-methylfluorene and 320 mg of fluorene, indicating conversion of 50 % of the original fluorene into its disubstituted derivative and 15 % into the monosubstituted derivative. This was a total yield of 57 %, based on methyl iodide or potassium metal.

d) Ethylation.

9-Fluorenylpotassium, prepared from fluorene (16.6 g, 0.1 mole) and potassium metal (3.9 g, 0.1 mole) in refluxing dioxane, was treated with ethyl bromide (10.9 g) at room temperature. Isolation of the reaction product by means of ether-water extraction yielded a yellow oil.

A sample of 452 mg of the product, separated on the chromatographic column, contained 142 mg of 9,9-diethylfluorene, 195 mg of 9-ethylfluorene and 118 mg of fluorene, indicating the conversion of 27 % of the original fluorene into its disubstituted derivative and 43 % into the monosubstituted derivative.

e) Allylation.

9-Fluorenylpotassium, prepared from fluorene (16.6 g, 0.1 mole) and potassium metal (3.9 g, 0.1 mole) in refluxing dioxane, was allowed to react with allyl bromide (12.1 g, 0.1 mole). The product was isolated as usual and a light yellow oil was obtained. A sample of 750 mg of the product, separated on the chromatographic column, consisted of about 250 mg

of 9,9-diallylfluorene, about 300 mg of 9-allylfluorene and about 200 mg of fluorene. This indicated the conversion of 27 % of the original fluorene into its disubstituted derivative and 40 % into the monosubstituted derivative.

f) Diethylation.

9-Fluorenylpotassium, prepared from fluorene (8.3 g, 0.05 mole) and potassium metal (3.9 g, 0.1 mole) in refluxing dioxane (80 ml), was treated with ethyl bromide (10.9 g, 0.1 mole). The reaction product, a yellow oil, was isolated by the usual procedure.

A sample of 1000 mg of the product, separated on the chromatographic column, consisted of about 500 mg of 9,9-diethylfluorene, 330 mg of 9-ethylfluorene and 170 mg of fluorene, indicating the conversion of 45 % of the original fluorene into diethylfluorene and 33 % into monoethylfluorene. The total yield of ethylated fluorene was 61 %, based on ethyl bromide or potassium metal.

9-Fluorenylpotassium in diethyl ether.

a) Methylation.

Fluorene (16.6 g, 0.1 mole) and potassium metal (3.9 g, 0.1 mole), cut into small pieces, were heated in 100 ml of diethyl ether at reflux temperature (35° C) for 18 hours. Apparently all the metal had reacted after this time

forming a brown precipitate and a light brown colored solution. The reaction with methyl iodide (14.2 g, 0.1 mole), added at room temperature, occurred readily.

A sample of 1010 mg of the product, separated on the chromatographic column, contained 221 mg of 9,9-dimethylfluorene, 427 mg of 9-methylfluorene and 362 mg of fluorene, indicating the conversion of 20 % of the original fluorene into its disubstituted derivative and 42 % into the monosubstituted derivative. Hence the extent of metalation was about 82 %.

When fluorene and potassium metal reacted in diethylether at room temperature a brown precipitate occurred. Methylation after a stirring period of 24 hours indicated metalation to an extent of about 60 %.

b) Benzylation.

9-Fluorenylpotassium, prepared from fluorene (16.6 g, 0.1 mole) and potassium metal (3.9 g, 0.1 mole) in refluxing dioxane, was isolated by filtration under nitrogen and then suspended in diethyl ether (100 ml). When benzyl chloride (12.7 g) was added slowly, a quick reaction occurred. The product, a yellow solid, was separated into colorless 9,9-dibenzylfluorene (8.5 g, m.p.=147° C) and a yellow solution by treatment with cold hexane, petroleum ether or ethanol. Evaporation of the solvent yielded a mixture of fluorene and 9-benzylfluorene. The isolation of 8.5 grams of 9,9-dibenzyl-

conversion of 25 % of the fluorene into its disubstituted derivative.

9-Fluorenylpotassium in hexane.

a) Methylation.

9-Fluorenylpotassium, prepared from 0.1 mole of fluorene and potassium metal in refluxing dioxane, was isolated and washed several times with dry hexane. A suspension of the organometallic compound in 100 ml of hexane was treated with methyl iodide (14.2 g, 0.1 mole). Extraction of the inorganic byproduct with water and subsequent evaporation of the hexane left a yellow oil.

A sample of 750 mg of the product, separated on the chromatographic column, contained 58 mg of 9,9-dimethylfluorene, 305 mg of 9-methylfluorene and 387 mg of fluorene, indicating the conversion of 7 % of the original fluorene into its disubstituted derivative and 40 % into the monosubstituted derivative.

b) Benzylation.

9-Fluorenylpotassium, prepared from 0.1 mole of fluorene and potassium metal in refluxing dioxane, was isolated and washed several times with dry hexane. To a suspension of the brown salt in about 100 ml of hexane, benzyl chloride (12.7 g) was slowly added. After completion of the reaction the product was isolated as usual. Evaporation of the hexane yielded

product was isolated as usual. Evaporation of the hexane yielded a yellow solid, which upon treatment with cold ethanol separated 9,9-dibenzylfluorene (2.9 g) from fluorene and 9-benzylfluorene.

9-Fluorenylpotassium in di-n-butyl ether.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were stirred at room temperature in di-n-butylether (50 ml) for a period of 24 hours. No significant reaction had occurred during this time. When fluorene and potassium metal were refluxed for 5 hours in di-n-butylether a brown crystalline precipitate was obtained. The reaction with an equivalent amount of methyl iodide occurred readily. The brown precipitate had occluded unreacted potassium metal. When a sample of 816 mg of the product was separated on a chromatographic column it yielded 5o mg of 9,9-dimethylfluorene, 150 mg of 9-methylfluorene and 616 mg of fluorene, indicating the conversion of 5 % of the original fluorene into its disubstituted derivative and 17 % into the monosubstituted derivative. The extent of metalation was 27 %.

Repetition of the experiment, allowing a reaction time of 12 hours, resulted in about 57 % of metalation. A sample of 1000 mg of the reaction product with methyl iodide contained about 1oo mg of 9,9-dimethylfluorene, 400 mg of 9-methylfluorene and 500 mg of unreacted fluorene, indicating the conversion of 9 % of the original fluorene into dimethylfluorene and 39 % into monomethylfluorene.

9-Fluorenylpotassium in di-isopropyl ether.

Fluorene (8.3 g, 0.0 5 mole) and potassium metal (1.95 g, 0.05 mole) were refluxed in di-isopropyl ether for a period of 5 hours. A brown precipitate had formed, interspersed with unreacted potassium metal. Reaction with methyl iodide (7.1 g, 0.05 mole) and examination of the product as usual revealed that 4 % of the original fluorene were converted into dimethylfluorene and 24 % into monomethylfluorene. The extent of metalation was 32 %.

9-Fluorenylpotassium in 1,2-dimethoxyethane.

When fluorene (8.3 g, 0.05 mole) and potassium (1.95 g, 0.05 mole) were put together into 1,2-dimethoxyethane (50 ml), a red compound formed immediately on the surface of the metal. A dark red solution was obtained within a few minutes. Since the reaction is exothermic a cooling bath was required when it was desired to perform the reaction at room temperature. All potassium had reacted within 2 hours yielding a clear red solution. The reaction was completed in less than 1 hour when reflux temperature was applied. Reaction with methyl iodide (7.1 g, 0.05 mole), followed by the usual isolation procedure, yielded a yellow oil.

A sample of 1100 mg of this product, separated on the chromatographic column, consisted of 380 mg of 9,9-dimethylfluorene, 300 mg of 9-methylfluorene and 330 mg of fluorene, indicating the conversion of 35 % of the original fluorene

into its disubstituted derivative and 30 % into the monosubstituted derivative. The metalation was complete in this experiment.

When methyl iodide was added to the solution of 9-fluorenylpotassium before all metal had reacted, a sample of 994 mg of the product contained 329 mg of 9,9-dimethylfluorene, 180 mg of 9-methylfluorene and 485 mg of fluorene, indicating the conversion of 30 % of the original fluorene into dimethylfluorene and 18 % into monomethylfluorene. The extent of metalation at this stage was 78 %.

9-Fluorenylpotassium in diethoxyethane.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were allowed to react in 1,2-diethoxyethane (50 ml). A red solution began to form as soon as the reagents were mixed. At room temperature all the metal had reacted within 3 hours. At reflux temperature the reaction was complete within 2 hours. A dark red solution was obtained. No precipitation of the organometallic compound occurred at room temperature. The 9-fluorenylpotassium was treated with methyl iodide (7.1 g, 0.05 mole) and the product isolated as usual.

A sample of 934 mg,separated on the chromatographic column, yielded 264 mg of 9,9-dimethylfluorene, 206 mg of 9-methylfluorene and 464 mg of fluorene, thus indicating a conversion of 26 % of the original fluorene into dimethylfluorene and 22 % into monomethylfluorene.

The extent of metalation was 74 %.

9-Fluorenylpotassium in tetrahydrofuran.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were allowed to react in tetrahydrofuran. A quick reaction occurred even at room temperature and a cooling bath was required when it was desired to perform the reaction at room temperature. Within 2.5 hours all the metal had reacted yielding a dark red solution. At reflux temperature all the metal reacted within 1 hour. The product of the reaction with methyl iodide, isolated as usual, was separated on the chromatographic column.

A sample of 532 mg consisted of 130 mg of 9,9-dimethylfluorene, 120 mg of 9-methylfluorene and 282 mg of fluorene , indicating the conversion of 22 % of the original fluorene into its disubstituted derivative and 22 % into the monosubstituted derivative. The extent of metalation was 66 %.

9-Fluorenylpotassium in hydrocarbons and mixed solvents.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were heated in refluxing toluene (50 ml) (b.p. 110°). A very small amount of 9-fluorenylpotassium had formed within 12 hours. The reaction with methyl iodide yielded 9-methylfluorene to an extent of less than 5 %. No fraction of pure 9-methylfluorene could be obtained by chromatographic separation. Replacement of toluene by xylene

(b.p. 138°) did not alter the results. The performance of the reaction in toluene, containing 1 % of dioxane, resulted in no noticeable improvement. Toluene containing 20 % of diethyl ether, di-n-butyl ether or di-isopropyl ether also was an inefficient solvent mixture.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole), heated in refluxing toluene containing 20 % dioxane, resulted in the formation of a reddish-brown solution, which slowly precipitated brown 9-fluorenylpotassium. After 5 hours' refluxing the reaction mixture, still containing unreacted metal, was cooled to room temperature and methyl iodide (7.1 g, 0.05 mole) was added.

A sample of 982 mg of the product, separated on the chromatographic column, yielded 55 mg of 9,9-dimethylfluorene, 380 mg of 9-methylfluorene and 527 mg of fluorene, indicating the conversion of 5 % of the original fluorene into dimethylfluorene and 38 % into monomethylfluorene. The extent of metalation was 48 %.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.39 g, 0.05 mole) were allowed to react in refluxing toluene (50 ml) containing 20 % of 1,2-dimethoxyethane. A reddish-brown solution soon formed, depositing 9-fluorenylpotassium slowly. After 2 hours' refluxing apparently all the metal had reacted and then methyl iodide (7.1 g, 0.05 mole) was added at room temperature.

A sample of 1016 mg of the product, separated on the chromatographic column, yielded 236 mg of 9,9-dimethylfluorene, 225 mg of 9-methylfluorene and 555 mg of fluorene, indicating the conversion of 21 % of the original fluorene into dimethylfluorene and 22 % into monomethylfluorene. The extent of metalation was 64 %.

Fluorene (8.3 g, 0.05 mole) and potassium metal (1.39 g, 0.05 mole) were heated in refluxing toluene containing 20 % of 1,2-diethoxyethane. The reaction started even at room temperature. After 4 hours' refluxing nearly all metal had reacted. Methyl iodide (7.1 g, 0.05 mole) was added to the reaction mixture. A sample of 918 mg, separated on the chromatographic column, yielded about 200 mg of 9,9-dimethylfluorene, 280 mg of 9-methylfluorene and 438 mg of fluorene, indicating the conversion of 20 % of the original fluorene into dimethylfluorene and 30 % into monomethylfluorene.

Fluorene (16.6 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were mixed in toluene (50 ml) containing 20 % tetrahydrofuran. After a period of 4 hours' refluxing only very little of the metal appeared to be unreacted. A reddish-brown solution was obtained, slowly depositing a fine brown precipitate, becoming heavy at room temperature. Methyl iodide (7.1 g, 0.05 mole) was added to the reaction mixture. A sample of 1168 mg of the product, separated on the chromatographic column, consisted of 156 mg of 9,9-dimethylfluorene, 325 mg of 9-methylfluorene and 687 mg of fluorene, indicating

the conversion of 12 % of the original fluorene into dimethylfluorene and 27 % into monomethylfluorene. The extent of metalation was 51 %.

Fluorene (16.6 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were allowed to react in heptane (50 ml) containing 20 % of 1,2-dimethoxyethane . A brown colored compound accumulated soon on the surface of the potassium metal. After 3 hours' refluxing all metal had reacted. Two liquid layers were observed when stirring was discontinued, the upper layer had a yellow color and consisted predominently of heptane. The lower one was dark red colored and contained 9-fluorenylpotassium and dimethoxyethane. Methyl iodide (7.1 g, 0.05 mole) was added to the reaction mixture, followed by the isolation procedure in the usual manner. A sample of 1168 mg of the product was separated on the chromatographic column and yielded 420 mg of 9,9-dimethylfluorene, 350 mg of 9-methylfluorene and 398 mg of fluorene, indicating the conversion of 33 % of the original fluorene into dimethylfluorene and 40 % into monomethylfluorene. The extent of metalation was 96 %.

Air decomposition of 9-fluorenylpotassium.

9-Fluorenylpotassium, prepared from fluorene (8.3 g) and potassium metal (1.95 g) in refluxing dioxane, was cooled to room temperature. The organometallic compound was separated by filtration and exposed to air for 12 hours, yielding

a black resin-like material which was treated with ether and water. The ether layer was evaporated and the remaining brown solid identified by infrared spectroscopy as a mixture of fluorenone, fluorenol and fluorene.

9-Fluorenylsodium in dioxane.

a) Methylation.

Fluorene (16.6 g, 0.1 mole) and powdered sodamide (3.9 g, 0.1 mole) were heated in refluxing dioxane (80 ml) for a period of 8 hours. A dark brown compound formed which was partly soluble in dioxane. Methyl iodide (14.2 g, 0.1 mole) was added to the reaction mixture at room temperature, followed by a one hour stirring period at room temperature. The product was isolated in the usual manner, yielding a yellow oil which slowly deposited unreacted fluorene.

A sample of 690 mg, separated on the chromatographic column, yielded 74 mg of 9,9-dimethylfluorene, 273 mg of 9-methylfluorene and 343 mg of fluorene, indicating the conversion of 10 % of the original fluorene into dimethylfluorene and 38 % into the monomethylfluorene. The extent of metalation was 52 %.

An attempt to bring about reaction between sodium metal (1.15 g, 0.05 mole) and fluorene (8.3 g, 0.05 mole) in refluxing dioxane (10 ml) for 8 hours yielded only a very small amount of brown 9-fluorenylsodium. The unreacted sodium was weighed, showing that only 4 % of the metal had reacted in this time.

b) benzylation.

9-Fluorenylsodium, prepared from fluorene (16.6 g, 0.1 mole) and powdered sodamide (3.9 g, 0.1 mole) in refluxing dioxane (80 ml) was treated with benzyl chloride (12.7 g, 0.1 mole) at room temperature. The product, a yellow crystalline solid, was isolated as usual by ether extraction. Treatment with cold ethyl alcohol separated 5.6 g of 9,9-dibenzylfluorene as white crystals, m.p. 148°. This yield indicates that 16 % of the original fluorene was converted into the disubstituted derivative.

9-Fluorenylsodium in 1,2-dimethoxyethane.

9-Fluorenylsodium, prepared from fluorene (16.6 g, 0.1 mole) and powdered sodamide (3.9 g, 0.1 mole) in refluxing dimethoxyethane (80 ml), was treated with methyl iodide (14.2 g, 0.1 mole). A sample of 1300 mg of the product was separated on the chromatographic column into about 200 mg of 9,9-dimethylfluorene, 500 mg of 9-methylfluorene and 600 mg of fluorene, indicating the conversion of 15 % of the original fluorene into dimethylfluorene and 40 % into monomethylfluorene. The extent of metalation was 70 % in this experiment.

Fluorene (8.3 g, 0.05 mole) and sodium metal (1.15 g, 0.05 mole), cut into small pieces, were allowed to react in 1,2-dimethoxyethane (50 ml). At room temperature all metal had reacted within 8 hours, forming a dark red solution. No precipitation of 9-fluorenylsodium occurred. At reflux temperature the

small pieces of sodium tended to stick together. The metal did not melt under these conditions. Within 10 hours all the metal had reacted.

The 9-fluorenylsodium prepared in this manner was treated with methyl iodide (7.1 g, 0.05 mole). A sample of 810 mg of the product, separated on the chromatographic column, yielded 300 mg of 9,9-dimethylfluorene, 260 mg of 9-methylfluorene and 250 mg of fluorene, indicating the conversion of 34 % of the original fluorene into dimethylfluorene and 32 % into monomethylfluorene. The metalation was complete. Repetition of the experiment yielded a product which consisted of 282 mg of 9,9-dimethylfluorene, 231 mg Of 9-methylfluorene and 336 mg of fluorene when a sample of 849 mg was subjected to chromatographic separation. This indicated a conversion of 30 % of the original fluorene into its disubstituted derivative and 27 % into the monosubstituted derivative. The extent of metalation was 87 %.

9-Fluorenylsodium in 1,2-diethoxyethane.

Fluorene (8.3 g, 0.05 mole) and sodium metal (1.15 g, 0.05 mole) were allowed to react in 1,2-diethoxyethane (50 ml). At room temperature the reaction was very slow. A red solution formed but after 50 hours some of the metal was still unreacted. At reflux temperature, where the metal is molten, the reaction was nearly complete within 30 hours. The product remained largely soluble at room temperature. 9-Fluorenylsodium,

prepared in this manner, was treated with methyl iodide (7.1 g, 0.05 mole). A sample of 1000 mg of this product, separated on the chromatographic column, yielded 190 mg of 9,9-dimethylfluorene, 400 mg of 9-methylfluorene and 410 mg of fluorene, indicating that 17 % of the original fluorene were converted into dimethylfluorene and 39 % into monomethylfluorene. The extent of metalation was 73 %.

9-Fluorenylsodium in tetrahydrofuran.

Fluorene (8.3 g, 0.05 mole) and sodium metal (1.15 g, 0.05 mole) were mixed in tetrahydrofuran (50 ml). At room temperature and at reflux temperature the reaction was very slow. A red solution formed but the metal was still unreacted to a large extent after 50 hours. No reaction with methyl iodide was performed.

9-Fluorenyllithium in dioxane.

Fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole) were heated in refluxing dioxane (50 ml). Within 4 hours no significant reaction occurred. More than 95 % of the metal was unreacted. The addition of 10 % of dimethoxyethane to the solvent changed the situation markedly. Soon after this addition a red colored solution was obtained. After 10 hours refluxing about 90 % of the metal had reacted . The 9-fluorenyllithium was largely soluble in this solvent and a very fine precipitate was observed at room temperature.

9-Fluorenyllithium in 1,2-dimethoxyethane.

Fluorene (8.5 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole) were mixed in dimethoxyethane (50 ml). A reaction occurred at room temperature, forming a red solution of 9-fluorenyllithium. At room temperature and reflux temperature all metal appeared to have reacted within 5 hours. The product, which remained dissolved at room temperature, was reacted with methyl iodide (7.1 g, 0.05 mole). A sample of 706 mg of the product was separated on the chromatographic column and yielded 40 mg of 9,9-dimethylfluorene, 576 mg of 9-methylfluorene and 90 mg of fluorene, indicating the conversion of 5 % of the original fluorene into its disubstituted derivative and 81 % into the monosubstituted derivative. The extent of metalation was 91 % in one case and 85 % in another run.

9-Fluorenyllithium in 1,2-diethoxyethane.

Fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole) were mixed in 1,2-dimethoxyethane (50 ml). The reaction occurred at room temperature and after a period of 50 hours of stirring about 80 % of the metal had reacted. A dark red solution was obtained, but a large amount of the 9-fluorenyllithium precipitated as an orange solid. At reflux temperature the reaction was completed within 5 - 6 hours. The 9-fluorenyllithium precipitated from the solution even at higher temperature.

Methyl iodide (7.1 g, 0.05 mole) was added to the reaction mixture. A sample of 920 mg of the product was separated on the chromatographic column and yielded 50 mg of 9,9-dimethylfluorene, 584 mg of monomethylfluorene and 286 mg of fluorene, indicating that 5 % of the original fluorene was converted into dimethylfluorene and 62 % into monomethylfluorene. The extent of metalation was 72 %.

9-Fluorenyllithium in tetrahydrofuran.

Fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole), cut into small pieces, were added to tetrahydrofuran (50 ml). At room temperature a very slow reaction occurred and after 4 hours the solution was red colored but most of the metal was still unreacted. After 50 hours the reaction appeared to be complete. At reflux temperature all metal had reacted after 7.5 hours. A clear red solution was obtained. To the reaction mixture was added methyl iodide (7.1 g, 0.05 mole). A sample of 591 mg of the product, analyzed on the chromatographic column, contained 11 mg of 9,9-dimethylfluorene, 504 mg of 9-methylfluorene and 76 mg of fluorene, indicating the conversion of about 2 % of the original fluorene into dimethylfluorene and 84 % into monomethylfluorene. The extent of metalation was 88 %.

9-Fluorenyllithium in hexane.

9-Fluorenlylithium prepared from fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole) in refluxing diethoxyethane was freed from the ether solvent by several

washings with hexane and finally suspended in 100 ml of hexane. Methyl iodide (7.1 g, 0.05 mole) was added to this suspension. When the product was separated on the chromatographic column, no disubstituted material was obtained. The yield of 9-methylfluorene was 83 % in one case, repetition of the experiment yielded 76 % 9-methylfluorene. Again, no dimethylfluorene was observed.

4. Metalation of Triphenylmethane and Diphenylmethane.

Triphenylmethane.

Triphenylmethane (12.2 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were refluxed in 50 ml of 1,2-dimethoxyethane. The solution showed a red color after 30 minutes and in 10 hours all the metal was consumed. To the deep red solution, containing the completely dissolved triphenylmethylpotassium, was added 6.3 g (0.05 mole) of benzyl chloride. The solution, which decolorized rapidly, was then diluted with 150 ml of water, extracted with ether and the ether extracts dried ($CaCl_2$). Removal of the ether gave a yellow solid which was triturated with pentane to remove unreacted triphenylmethane. Colorless 1,1,1,2-tetraphenylethane requiring no further purification was obtained in good yield, m.p. 140° uncorr., lit. 140 - 142° (64).

When sodium replaced potassium in a similar experiment a light red color developed only after 12 to 15 hours

of reflux. The small pieces of sodium had formed a single spherical piece of metal. After 100 hours of reflux, 99 % of the metal (by weight) remained unreacted. Lithium showed red coloration of the surface of the metal in 5 hours, but gave only 10 % reaction of the metal after 100 hours reflux.

Diphenylmethane.

Details for the reaction between diphenylmethane and potassium followed those described for the triphenylmethane. Evidence of the reaction, via appearance of a red color in the solution, occurred within 3 hours. In 3 days, nearly all the potassium had disappeared giving a product quite soluble in DME. Treatment of the salt with benzyl chloride gave 1,1,2-triphenylethane, m.p. 53°, lit. 54° (65).

Lithium, under the same conditions formed only a small amount of red precipitate on the metal surface but no change occurred after 30 hours of reflux.

5. Deuteration Experiments.

Preparation of KOD and LiOD.

Into 100 ml of dry hexane was pipetted one ml of 98 % D_2O. A piece of freshly cut potassium, in excess of the amount required to react with all the D_2O, was suspended on a length of wire and immersed in the hexane and cautiously allowed

to touch the surface of the D_2O at the bottom of the flask and then was immediately withdrawn but not removed from the hexane. This "dipping" process was repeated until a coating of KOD was developed on the surface of the metal. The reaction was quite vigorous at first but soon moderated. The solid was allowed to remain overnight in the flask in contact with the small amount of D_2O in the lower layer. The KOD was then removed from the metal and, following the elimination of hexane, was weighed for use.

LiOD was prepared by a similar manner but required somewhat longer contact with the traces of D_2O for complete reaction.

Hydrogen - deuterium exchange with LiOD.

a) Fluorene (1.66 g, 0.01 mole) and LiOD (250 mg, 0.01 mole) were refluxed for 1 hour in dry dioxane (5 ml). LiOD did not dissolve under these conditions. The product was separated by addition of ether and water to the dioxane solution. The ether layer was dried and evaporated. The product was recrystallized from alcohol before the infrared spectrum was obtained. The spectrum had no indication of deuterated fluorene.

b) Repetition of the experiment (a) using 1,2-dimethoxyethane (5 ml) as the solvent yielded the same result. Only unchanged fluorene was isolated.

c) Fluorene (1.66 g, 0.01 mole), LiOD (250 mg, 0.01 mole) and D_2O (200 mg, 0.01 mole) were refluxed for 1 hour in 1,2-dimethoxyethane (5 ml). Separation of fluorene from solvents and inorganic materials was done by use of ether and water. The resulting yellowish white product was recrystallized from alcohol. From the I R spectrum it could be concluded that about 10 % C_9 -monodeuterated fluorene were formed.

d) Fluorene (1.66 g, 0.01 mole) and LiOD (250 mg, 0.01 mole) were refluxed for 1 hour in 1,2-dimethoxyethane (5 ml) containing D_2O (0.5 ml). The LiOD remained undissolved. The usual isolation procedure yielded fluorene which contained about 15 % of C_9 -monodeuterated fluorene as shown by the infrared spectrum.

<u>Hydrogen - deuterium exchange with KOH and D_2O.</u>

a) Fluorene (1.66 g, 0.01 mole), KOH (560 mg, 0.01 mole) and D_2O (200 mg, 0.01 mole) were refluxed in pure dioxane (5 ml) for 1 hour. The potassium hydroxide dissolved under these conditions to form a clear solution. The product was isolated by the usual ether-water treatment, followed by recrystallization from alcohol. The infrared spectrum indicated that the product consisted of about 90 % of unchanged fluorene and 10 % of C_9 -monodeuterated fluorene. No C_9 -dideuterated fluorene was observed.

b) Repetition of experiment (a), but using 8 ml of dioxane and allowing 3 hours for reaction, produced 5 - 8 % C_9 -monodeuterated fluorene.

c) Fluorene (1.16 g, 0.01 mole), KOH (60 mg, 0.01 mole) and D_2O (200 mg, 0.01 mole) were refluxed in 1,2-dimethoxyethane for 1 hour. The potassium hydroxide dissolved readily during the reaction. The product, isolated as usual, consisted of three components, fluorene, mono- and dideuterated fluorene, the relative amounts of which could be estimated to 45 : 50 : 5 respectively.

Hydrogen - deuterium exchange with KOD.

a) Fluorene (1.66 g, 0.01 mole) and KOD (561 mg, 0.01 mole) were refluxed in dry dioxane (5 ml). The KOD remained undissolved in this anhydrous solvent. The infrared spectrum of the product, isolated and purified as usual indicated that 30 % of the fluorene became converted to monodeuterated fluorene in the 1 hour allowed for reaction.

b) Repetition of experiment (a) but using 8 ml of dioxane solvent produced 10 - 15 % deuterated fluorene. Again the KOD was not dissolved in the solvent.

c) Experiment (b), extented for 3 hours reaction time resulted in formation of approximately 40 % deuterated fluorene.

d) Fluorene (1.16 g, 0.01 mole) and KOD (561 mg, 0.01 mole) were refluxed in dry 1,2-dimethoxy ethane.

The KOD was not dissolved under the reaction conditions. After 1 hour reaction a product was isolated which consisted of fluorene, mono- and dideuterated fluorene in relative amounts of 45 : 50 : 5 respectively.

Hydrogen - deuterium exchange with KOD and D_2O.

a) When fluorene (1.16 g, 0.01 mole) and KOD (561 mg, 0.01 mole) were refluxed in 1,2-dimethoxyethane (5 ml), containing one equivalent of D_2O (200 mg), all the KOD dissolved under these conditions. The red color of the 9-fluorenyl-anion was observed within the first few minutes of the reaction, but disappeared as the reaction proceeded. After one hour reaction time the product was isolated and purified as usual. The infrared spectrum showed that half of the product was monodeuterated fluorene. This was accompanied by dideuterated fluorene (30 %) and a smaller amount of unchanged fluorene (20 %).

b) Repetition of experiment (a), with dioxane as solvent, also resulted in a clear solution. The product contained fluorene, mono- and dideuterated fluorene in relative amounts of 15 : 45 : 40 respectively.

Deuteration of 9-fluorenylpotassium.

a) Fluorene (1.66 g, 0.01 mole) and potassium metal (0.39 g, 0.01 mole) were refluxed for 3 hours in dry dioxane (5 ml). A dark red solution was obtained. All of the potassium appeared to have reacted after that time.

The brown solution was cooled to room temperature and an excess of D_2O (1 ml) was added. Stirring was continued for 1 hour at room temperature. The reaction product was isolated by the usual ether-water treatment. Recrystallization from alcohol yielded a product melting at 110°. The infrared spectrum showed the presence of mono- and dideuterated fluorene. Their relative amounts were about 60 : 40. Unchanged fluorene was present only in traces, certainly not more than 2 %.

b) Experiment (a) was repeated but this time an equivalent amount of D_2O (200 mg, 0.01 mole) was added, the reaction mixture again stirred for 1 hour at room temperature. The product consisted of 35 % of unchanged fluorene, 50 % of C_9 -monodeuterated fluorene and 15 % of C_9 -dideuterated fluorene.

c) Fluorene (1.66 g, 0.01 mole) and potassium metal (0.39 g, 0.01 mole) were refluxed in dry 1,2-dimethoxyethane for a period of 20 minutes by which time all the potassium had reacted. A clear, dark-red solution was formed. D_2O (200 mg, 0.01 mole) was added at room temperature and then stirring was continued for 1 hour. The product was isolated as usual. It consisted of fluorene (15 %), C_9 -monodeuterated fluorene (45 %) and C_9 -dideuterated fluorene (40 %), as estimated from the infrared spectrum.

<u>Deuteration of 9-fluorenylsodium.</u>

Fluorene (8.3 g, 0.05 mole) and sodium metal

(1.15 g) were refluxed in dry 1,2-dimethoxyethane (50 ml). After 36 hours all of the sodium appeared to have reacted. D_2O (1.0 g, 0.05 mole) was then added. Reaction occurred immediately. After the mixture was stirred for 1 hour, the isolation of the product followed the usual way. The infrared spectrum showed that about 5 % of the fluorene had not reacted and the amount of dideuterated fluorene was slightly higher than that of the monodeuterated fluorene.

Deuteration of 9-fluorenyllithium.

a) Fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole), cut into small pieces of about 1 mm^3, were refluxed in pure dry 1,2-dimethoxyethane. After 5 hours of reaction when all lithium appeared to have reacted, the reaction mixture was cooled to room temperature and D_2O (1.0 g, 0.05 mole) was added, followed by one hour of stirring at room temperature. The product, isolated as usual, contained about 80 % of C_9 -monodeuterated fluorene, accompanied by fluorene and dideuterated fluorene, the amount of the former slightly predominating.

b) The deuteration of 9-fluorenyllithium in hexane has been recorded under the preparation of the samples for the infrared work.

6. Reaction of Alkali Metal Derivatives of Fluorene and 9-Benzoylfluorene with Benzoyl Chloride and Ethyl Benzoate.

The reaction of 9-fluorenylpotassium with benzyl chloride.

a) in dioxane. Fluorene (16.6 g, 0.1 mole) and potassium (3.9 g, 0.1 mole) were kept for 4 hours in 160 ml of pure, dry dioxane at reflux temperature. Under these conditions all the potassium was consumed. The mixture was allowed to cool to room temperature and then benzyl chloride (14 g, 0.1 mole), dissolved in 50 ml of dioxane, was slowly added. The dark red color of the original solution turned to light orange and a viscous solution was formed. Addition of ether and water followed by several washings of the ether layer with water permitted removal of the inorganic salts and the dioxane. At room temperature the ether layer contained yellow crystals which were separated. A second crop of crystals was obtained when the mother liquor was reduced in volume. The yield of crude material was 11.7 g (31 %). After unchanged fluorene and 9-benzoylfluorene were removed by trituration with hot ethyl alcohol, there was obtained pure 9-1'-benzoylbenzylidenefluorene, m.p. 189° .

b) in pentane. Fluorene (8.3 g, 0.05 mole) and potassium metal (1.95 g, 0.05 mole) were kept for 4 hours in 40 ml of pure, refluxing dioxane. The cooled solution, containing no unreacted potassium, was poured into 500 ml of dry pentane, whereupon the 9-fluorenylpotassium precipitated. The

The liquid was decanted and the precipitate was washed by decantation using pentane, and then suspended in 100 ml of pentane. To this was added slowly a solution of 7 g (0.05 mole) of benzoyl chloride in 50 ml of dry pentane. Reaction occurred immediately but was allowed to continue for 3 hours with stirring to assure maximum reaction of the suspended solid. After removal of inorganic substances by water washes, there remained a solid material suspended in the pentane layer. When this was removed and dried it weighed 9.9 g. Contaminating fluorene and 9-benzoylfluorene were removed by extraction of the crude material with hot ethanol in which both the 9-1'-benzoyloxybenzylidene-fluorene and 9,9-dibenzoylfluorene are insoluble. There was obtained 5.1 g (27 %) of material analyzing correctly for the enol ester and melting at 180° C.

The pentane mother liquor, upon evaporation yielded a small amount of 9-benzoylfluorene and a considerable quantity of unreacted fluorene.

<u>The reaction of 9-fluorenylpotassium with ethyl benzoate.</u>

a) <u>in dioxane.</u> To the product obtained from the reaction of 8.3 g (0.05 mole) of fluorene and 1.95 g (0.05 mole) of potassium in 40 ml of dioxane was added 7.5 g (0.05 mole) of ethyl benzoate in 10 ml of dioxane. The addition could be made rapidly since the reaction was slow.
The solution was stirred overnight at room temperature.

The dark brown color of the solution did not change during the reaction. The product was isolated by addition of water and ether to the cooled reaction mixture. The ether layer was freed of solvent and left 11.5 g of a yellow, oily solid. This material dissolved in alcohol deposited 5.2 g (39 %) of pure 9-benzoylfluorene, m.p. 135°C. Identification was corroborated by mixed melting point and by comparison of its infrared spectrum with that of an authentic specimen (37).

b) <u>in pentane.</u> Fluorene (8.3 g) was converted to 9-fluorenylpotassium as above. The dioxane solution of the salt was poured into dry pentane. The brown precipitate was washed free of dioxane by decantation, using dry pentane, and then suspended in 100 ml of pentane. A pentane solution of 7.5 g of ethyl benzoate was then added to the suspension. The slow reaction was allowed to proceed overnight, aided by continual stirring. Inorganic materials were removed by shaking the pentane mixture with water. The pentane solution contained 2.2 g of solid 9-benzoylfluorene which was removed by filtration. Evaporation of the pentane from the mother liquor gave an oily product which afforded a further quantity of 3.4 g of 9-benzoylfluorene. Yield 5.6 g, 42 %.

<u>The reaction of 9-fluorenyllithium and benzoyl chloride.</u>

A) <u>in 1,2-diethoxyethane.</u> Fluorene (8.3 g, 0.05 mole) and lithium metal (350 mg, 0.05 mole) were allowed to react for 5 hours in 40 ml of pure, dry 1,2-diethoxyethane.

To the solution, containing no unreacted metal, and cooled to room temperature, was added 7.0 g (0.05 mole) of benzoyl chloride dissolved in the same solvent. Slow addition was necessary due to the rapidity of the reaction.
The reaction mixture was stirred for 1 hour to permit completion of the reaction. The addition of ether and water gave 6.0 g of a yellow solid, insoluble in the ether. This material, extracted several times with hot ethanol to remove unreacted fluorene and any 9-benzoylfluorene, melted at 158° - 159° and proved to be a mixture of 9-1'-benzoyloxybenzylidenefluorene and 9,9-dibenzoylfluorene. All attempts at separation failed due to the insolubility of both compounds in suitable reagents. That this product was a mixture of enol ester and β-diketone was shown by comparison of the infrared spectra of the pure enol ester and the diketo compound as well as their mixtures with the spectra of the product from this reaction.

b) <u>in pentane.</u> Fluorene (8.3 g) was converted to 9-fluorenyllithium as above. The reaction mixture was poured into pentane whereupon all of the organometallic compound precipitated as an orange solid. The solid was washed twice with pentane and after suspension in 100 ml of pentane, was treated with 7.0 g of benzoyl chloride dissolved in a small amount of pentane. Reaction occurred readily and the orange color disappeared within a few minutes. The mixture was stirred for 3 hours at room temperature to ensure complete reaction.
After a water wash, the dried pentane solution gave

5.5 g (28 %) of yellow solid melting at 182°. This was identified as 9,9-dibenzoylfluorene both by mixed melting point and infrared spectra using an authentic sample (34).

The reaction of 9-fluorenyllithium and ethyl benzoate.

a) in 1,2-diethoxyethane. Fluorene (8.3 g) was converted to 9-fluorenyllithium as before. The reddish mixture was cooled to room temperature and treated with 7.5 g of ethyl benzoate also dissolved in 1,2-diethoxyethane. The mixture was stirred at room temperature overnight. The addition of ether and water caused no precipitation. The ether layer, washed with water and dried, yielded upon removal of the ether a solid which proved to be a mixture of 9-benzoylfluorene and fluorene only. Separation of the 9-benzoylfluorene was accomplished by solution of the product in ethyl alcohol and subsequent crystallization, m.p. 135° ; yield 6.1 g, 45 %. The infrared spectra of the crude product failed to show bands characteristic of the enol ester or diketone.

b) in pentane. Fluorene (8.3 g) was converted to 9-fluorenyllithium as above. The mixture was then poured into dry pentane. The precipitated solid was then washed twice with pentane by suspension of the solid in the liquid followed by decantation after the solid had settled. To a suspension of this 9-fluorenyllithium in 100 ml of pentane was added 7.5 g of ethyl benzoate. The solution was stirred overnight

to ensure maximum reaction. The addition of water caused precipitation of 5.5 g (41 %) of a yellow solid which proved to be pure 9-benzoylfluorene. Evaporation of the pentane mother liquor yielded unreacted fluorene and an additional amount of 9-benzoylfluorene. No dibenzoylated fluorene was found.

The reaction of 9-benzoyl-9-fluorenyllithium with benzoyl chloride.

a) in 1,2-diethoxyethane. A mixture of 2.7 g (0.01 mole) of 9-benzoylfluorene and 70 mg (0.01 mole) of lithium metal was kept in refluxing 1,2-diethoxyethane (10 ml) for two hours. Within ten minutes the solution became light red due to the formation of the lithium salt. Complete reaction occurred after the two hour reflux period. An orange precipitate accumulated toward the end of the reaction, but the surface of the lithium metal showed no evidence of deposition of 9-benzoyl-9-fluorenyllithium. When the reaction mixture was cooled to room temperature more precipitation occurred. Benzoyl chloride (1.4 g, 0.01 mole) dissolved in 5 ml of 1,2-diethoxyethane was added and produced a rapid reaction. The mixture was then stirred at room temperature for 30 minutes. Addition of water and ether caused the separation of yellow crystals. Trituration of this solid with hot ethyl alcohol removed unreacted 9-benzoylfluorene.There remained 2.5 g (67 %) of an insoluble material whose analysis and infrared spectrum showed it to be a mixture of 9-1'-benzoyloxybenzylidene-fluorene and 9,9-dibenzoylfluorene.

b) <u>in dimethoxyethane.</u> 9-Benzoylfluorene (2.7 g) and lithium (70 mg) were allowed to react in refluxing 1,2-dimethoxyethane (10 ml) for 24 hours. Within 15 minutes of the beginning of the reaction the solution became red. A yellowish precipitate formed and coated the surface of the metal as the reaction proceeded. Even after 24 hours in the refluxing ether some unreacted metal remained. After this time the solution was cooled to room temperature and 1.4 g (0.01 mole) of benzoyl chloride in 5 ml of dimethoxyethane was added. Reaction occurred readily and was allowed to continue with stirring for one hour. The addition of ether and water caused the precipitation of a yellow solid which gave 2.1 g (56 %) of a mixture of 9,9-dibenzoylfluorene and 9-1'-benzoyloxybenzylidenefluorene after trituration with hot ethyl alcohol. The ether layer yielded unreacted 9-benzoylfluorene.

c) <u>in pentane.</u> The compound 9-benzoyl-9-fluorenyllithium was prepared in diethoxyethane from 2.7 g of 9-benzoylfluorene as described above. Addition of the resulting mixture to dry pentane precipitated all of the organometallic product. The lithium salt, freed from the ether by decantation and further pentane washes, was suspended in 50 ml of pentane and treated with 1.4 g (0.01 mole) of benzoyl chloride in pentane. The mixture was stirred for one hour and then poured into water. The yellowish solid which appeared was removed and triturated with hot ethyl alcohol to remove contaminating

9-benzoylfluorene. There was obtained 2.0 g (54 %) of the alcohol-insoluble 9,9-dibenzoylfluorene, m.p. 182°, identified further by its infrared spectrum.

The reaction of 9-benzoyl-9-fluorenyllithium with ethyl benzoate.

The compound 9-benzoyl-9-fluorenyllithium, prepared as above, when left in the ether solvent or suspended in pentane and treated with an equimolar quantity of ethyl benzoate, yielded only 9-benzoylfluorene, m.p. 135°.

The reaction of 9-benzoyl-9-fluorenylsodium with benzoyl chloride.

a) in 1,2-dimethoxyethane. 9-Benzoylfluorene (2.7 g, 0.01 mole) and sodium metal (230 mg, 0.01 mole) were allowed to react in 10 ml of refluxing 1,2-dimethoxyethane. Within two hours all the metal appeared to have reacted yielding a dark red solution. When the solution was cooled to room temperature very little precipitate occurred. The slow addition of 1.4 g (0.01 mole) of benzoyl chloride in 5 ml of dimethoxyethane produced a vigorous reaction with disappearance of the color. After an additional 30 minutes of stirring the mixture was diluted with ether and water. The insoluble precipitate was triturated with hot alcohol and gave 2.2 g (60 %) of pure 9-1'-benzoyloxybenzylidenefluorene. Unreacted 9-benzoylfluorene was obtained from the ether layer.

b) in diethoxyethane. The same reaction was performed but in diethoxyethane and followed a course identical with that above, yielding only the enol ester and unreacted 9-benzoylfluorene.

The reaction of 9-benzoyl-9-fluorenylsodium with ethyl benzoate.

When 9-benzoyl-9-fluorenylsodium was prepared in dimethoxyethane as above and treated with an equimolar amount of ethyl benzoate, the only product obtained, following the usual method of isolation, was unchanged 9-benzoylfluorene.

The reaction of 9-benzoyl-9-fluorenylpotassium.

a) with benzoyl chloride in 1,2-dimethoxyethane. 9-Benzoylfluorene (2.7 g, 0.01 mole) and potassium metal (390 mg, 0.01 mole) were heated for 30 minutes in 10 ml of refluxing 1,2-dimethoxyethane. The dark red solution, when cooled to room temperature, gave no precipitate. When benzoyl chloride (1.4 g, 0.01 mole) in 5 ml of 1.2-dimethoxyethane was added slowly, a rapid reaction occurred. After an additional 30 minutes of stirring the mixture was diluted with ether and water. The insoluble precipitate, after treatment with hot ethyl alcohol, afforded 1.8 g (48 %) of pure 9-1'-benzoyloxybenzylidenefluorene. Unchanged 9-benzoylfluorene was recovered from the ether layer.

b) <u>with ethyl benzoate in 1,2-dimethoxyethane</u>.

9-Benzoyl-9-fluorenylpotassium prepared as above, when treated with an equimolar amount of ethyl benzoate gave only unchanged 9-benzoylfluorene.

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